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19 KEY WORDS (Continue on reverse side if necessary and identify by block number)

High Energy Materials.
Nitrogen organic compounds.
Preparations and Procedures.

20 ABSTRACT (Continue on reverse side if necessary and identify by block number)

Our discovery of the oxidation of benzofuroxans into dinitrobenzene derivatives was investigated(three publications).

Investigations on oxidations designed to prepare dinitromaleonitrile led to other results(four publications).

Under controlled conditions the explosive mixture of hydrazine and dicyanofuraxan(U.S. pat. 3,740,947 and 3,832,249) gave an excellent yield of a diaminopyridazinofuroxan and a similar reaction with hydroxylamine gave an oxazinofuroxan(one publication).

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Diels-Ader reactions of the pyrrole ring are virtually unknown. An investigation(unsuccessful) of one route to dinitromaleonitrile led to a facile D.A. addition between a pyrrole and tetracyanoethylene(one publication).

An evaluation of methods for the preparation of secondary nitramines (particularly from tertiary aliphatic amines) led to an investigation of the preparation of secondary nitrosamines from tertiary aliphatic amines and a mixture of nitric and hydrochloric acids(first reported by Japanese). This work is continuing. Oxidation of nitrosamines into nitramines continues to be under investigation.

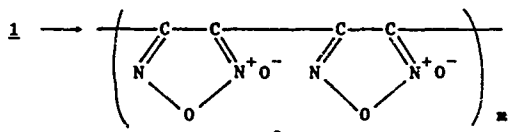
$C_{2n}N_{2n}O_{2n}$ Systems. Proximate Nitro and Cyano Groups.

An interest in $C_{2n}N_{2n}O_{2n}$ molecules as energy sources and explosives can be attributed, in part, to an exothermic formation of gases brought about by an irreversible bond redistribution, e.g., $C_{2n}N_{2n}O_{2n} \longrightarrow 2n\ CO + n\ N_2$ + energy. Dinitrosoacetylene 1, a representative of the family with n = 1, is unstable (isolated at - 80°C) and is also known as the di-N-oxide of cyanogen.[1] Apparently isomers, e.g., O=C=NN=C=O and ON≡CN=CO, are unknown.

$$O{=}NC{\equiv}CN{=}O \longleftrightarrow O^{-}N^{+}{\equiv}C{-}C{\equiv}N^{+}O^{-}$$

1

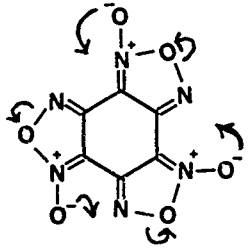
N-oxides of organic cyanides dimerize readily into furoxans. So, polymeric furoxans 2 (unknown) are, in principle, polymers of compound 1.



2

Although benzofuroxan 3 has not been prepared from compound 1, it is a trimer, $C_6N_6O_6$. High energy and explosive properties of compound 3 have been investigated; but it appears to be too unstable for practicable application.[2,3] All isomers of $C_6N_6O_6$, e.g. 3 and 4 (unknown) are expected to produce gases and energy by irreversible bond redistribution. By a simple bond redistribution, sets of six equivalent C atoms, six equivalent nitrogen atoms, and six equivalent oxygen atoms are present in compound 3; a

similar property for compound 4 can account for a set of six equivalent oxygen atoms (curved arrows indicate the redistribution).



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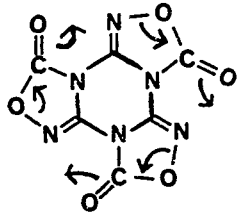
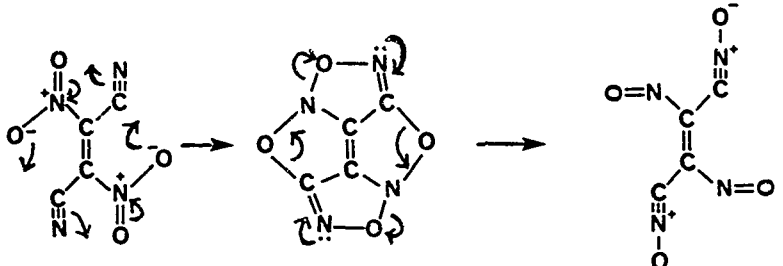


4

Other bond redistributions in $C_{2n}N_{2n}O_{2n}$ are also expected to occur thermally. By this simple process an isomerization of dinitrofumaronitrile 5 (unknown) into the di-N-oxide 7 (unknown) of dicyanofuroxan (both 5 and 7 are examples of $C_4N_4O_4$) is expected.



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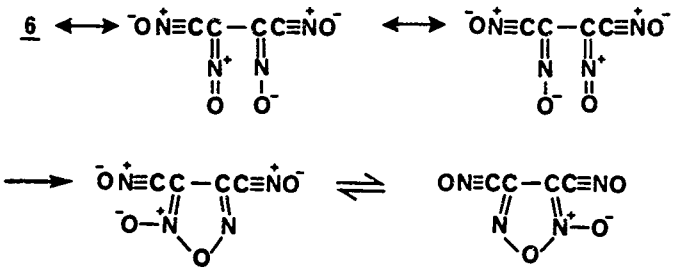

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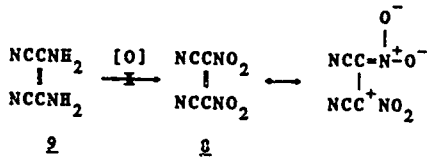
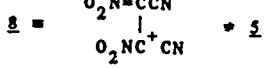
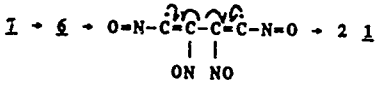
Since dinitrofumaronitrile 5 may also thermally equilibrate with dinitomaleonitrile 8, difficulty in isolating a discreet molecular species in our unsucessful attempts (see Parts II, VII, and IX) to obtain compound 8 by oxidation of diaminomaleonitrile 9 (readily available from hydrogen cyanide) can now be appreciated. In addition to the bond redistribution reactions, compounds 7 can polymerize, cf., 2, and depolymerize into the unstable compound 1.

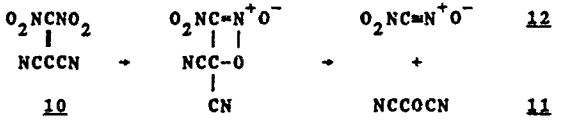


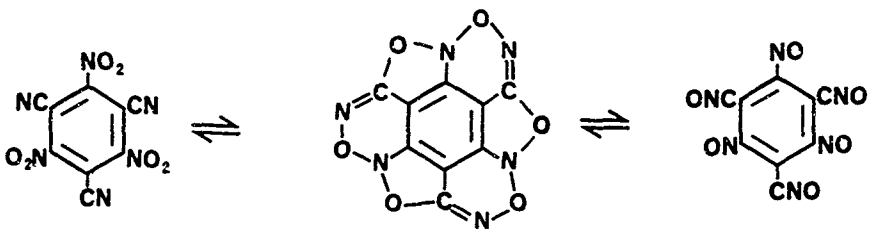
9 8





Since dinitromethylidene malononitrile 10 (unknown) may be less susceptible (than is now presumed for its isomers 5 and 8) toward bond redistribution reactions, its synthesis is proposed. That the nitrile 10 may be susceptible to ring-closure[4] followed by dissociation into oxomalononitrile 11 and nitroformonitrile oxide 12 is recognized. A related bond redistribution may interchange 1,3,5-tricyano-2,4,6-trinitrobenzene 13 into its tris-oxide 14 (both unknown). The latter would surely polymerize.

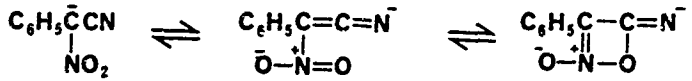




13 14

14 ⟶ Complex polymers.

In an anion of an α-nitronitrile there is also the opportunity for interaction between the functional groups. With cleavage into an isocyanate anion and a nitrile oxide this can account for the hitherto unexplained formation of benzonitrile oxide (isolated as its dimer, diphenylfuroxan 15) and trityl isocyanate 16 when the silver salt 17 of α-nitrobenzyl cyanide was treated with trityl chloride.[5]



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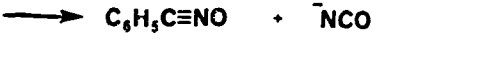

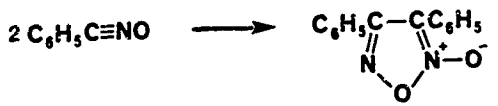

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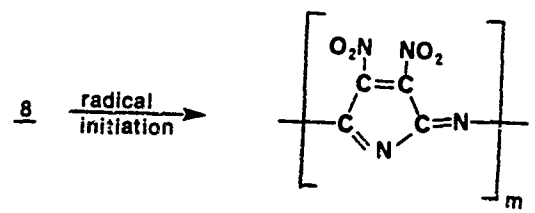
16

At the present time there are no known examples of the system $C_{2n}N_{2n}O_{2n}$ for n > 3 (furoxan polymers 2 are unknown). A polymeric dinitropyrrolonimine 17 formally represents self-addition of the two cyano groups in compound 8 (it is, of course, isomeric with a polyfuroxan 2). A reaction initiated by radicals or anions is proposed.[6,7]

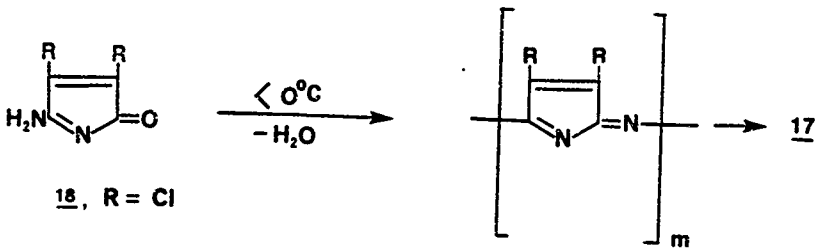


17

On the other hand, compound 8, because of its presumed instability, may be precluded as a precursor to its polymer 17 (expected to be stable). Fortunately there are, in principle other routes to the polymer. Replacement of chlorine atoms in

either 2-amino-3,4-dichloropyrrol-5-one 18 or its polymer 19 (both compounds are known)[8] by nitro groups will be investigated as a source of the polymer 17.

In this work (see Part IX) two routes to triaminopyrrolone 20 have been developed. An investigation on the preparation of polymeric diaminopyrrol-5-one 21 and its oxidation into the polymer 17 is planned. The necessity for the protection of amino groups by temporary derivitization is, of course, envisaged.



18, R = Cl

20, R = NH_2

19, R = Cl

21, R = NH_2

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BICYCLIC PEROXIDES FROM A 1,4-DIAZEPINE

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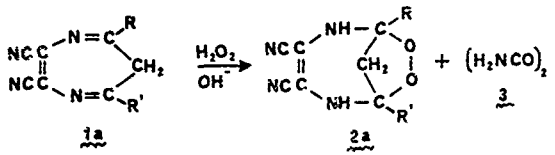
Chicago Circle Campus, Chicago, Illinois 60680 U.S.A.

Abstract - An adduct, 3,4-dicyano-1,6-dimethyl-2,5-diaza-7,8-dioxabicyclo[4.2.1]non-3-ene, was obtained from 2,3-dicyano-5,7-dimethyl-6H-1,4-diazepine and hydrogen peroxide in the presence of alkali or a tertiary amine. It was dehydrogenated by iodobenzene diacetate into 3,4-dicyano-1,6-dimethyl-2,5-diaza-7,8-dioxabicyclo[4.2.1]nona-2,4-diene; further oxidation by m-chloroperbenzoic acid gave 4,5-dicyano-1,8-dimethyl-2,7-diaza-3,6,9,10-tetraoxatetracyclo[6.2.1.$0^{2,5}$.$0^{5,7}$]undecane.

Hydrogen peroxide in the presence of sodium hydroxide or pyridine in methanol, or hydrogen peroxide in acetonitrile efficiently transformed 2,3-dicyano-5,7-dimethyl-6H-1,4-diazepine 1a[1] into 3,4-dicyano-1,6-dimethyl-2,5-diaza-7,8-dioxabicyclo-[4.2.1]-non-3-ene 2a,[2] the first example of a bicyclic peroxide from a diazepine. Oxamide was a minor by product. In the absence of an alkali or an amine the reaction in methanol gave traces of the adduct 2a and larger amounts of oxamide and 2,4-pentanedione. Peracids, e.g., m-chloroperbenzoic(MCPBA) or trifluoroperacetic acids, either failed to react with the diazepine 1a under mild conditions or gave intractable mixtures under more severe conditions. The detection of an isocyanide odor during peroxidation of diazepine 1a is being investigated.



1a → (H₂O₂, OH⁻) → 2a + (H₂NCO)₂ (3)

a, R = R' = CH_3; b, R = R' = C_6H_5; c, R = C_6H_5, R' = CH_3

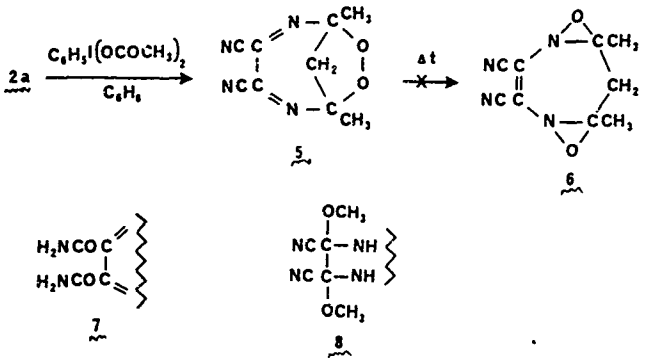
Anticipated reactions between a hydroperoxide and a diazepine apparently did not occur since neither an oxaziridine,[1-3] a nitrone,[3] an amide (other than oxamide),[4] simple ring cleavage,[7] nor ring contraction[8] was detected. The formation of oxamide 3, was attributed to the hydration of cyanogen,[9] a degradation intermediate, by aqueous peroxide. Attempts to obtain peroxides 2b,c from diazepines 1b,c and to obtain 2,3-dicyano-5,6,6,7-tetramethyl-6H-1,4-diazepine from 3,3-dimethylpentane-2,4-dione and diaminomaleonitrile by an adaptation of the preparation of the azepine 1a[1] were unsuccessful.

The peroxide structure 2a was directly supported by ir spectroscopic detection of NH, C≡N and C=C functions, by ^{1}H and ^{13}Cnmr detection of methyl and methylene protons and carbon atoms in CH_3, CH_2, CO and CN functions; by molecular weight determination and by elemental analysis. On standing in methanol(25°C, 90 hours), or on heating neat above 125°C (dec) the peroxide 2a fragmented into 2,4-pentanedione and presumably diiminosuccinonitrile 4, a precursor to cyanogen and oxamide 3. The latter was also obtained(47%) from the cyclic peroxide 2a and hydrogen peroxide in methanol (25°C, two days). Triphenylphosphine converted the peroxide 2a into the diazepine 1a.

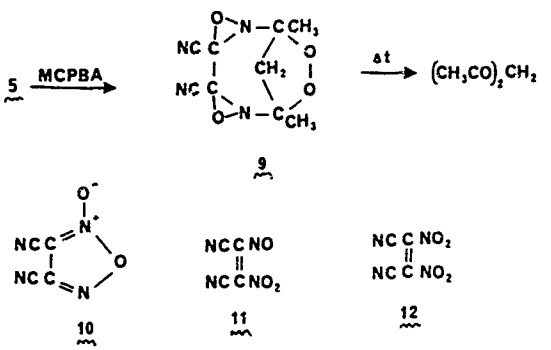
$$(CH_3CO)_2CH_2 + \underset{4}{\left[(HN{=}C(CN))_2\right]} \xleftarrow{\Delta\,t} \underset{2a}{} \xrightarrow{(C_6H_5)_3P} \underset{1a}{} + (C_6H_5)_3PO$$

$$\underset{2a}{} \xrightarrow[25^{\circ}C,\ 48\ h]{CH_3OH,\ H_2O_2} \left[\underset{4}{} \xrightarrow{-2\,HCN} (CN)_2\right] \xrightarrow[H_2O_2]{H_2O} \underset{3}{}$$

Iodobenzene diacetate in benzene quantitatively dehydrogenated the peroxide 2a into 3,4-dicyano-1,6-dimethyl-2,5-diaza-7,8-dioxabicyclo[4.2.1]nona-2,4-diene 5. (see Experimental Section for confirmation data). Without a trace of isomerization into a bisoxaziridine 6, thermolysis again gave 2,4-pentanedione but the remaining mixture was intractable. During chromatographic separation from silica gel hydration of the dicyanide 5 gave the diamide 7, whereas an azomethine adduct 8 was obtained from methanol containing sulfuric acid. The diazepine 1a was produced in small amounts from the peroxide 5 and triphenylphosphine.



m-Chloroperbenzoic acid(MCPBA) converted the bisimine 5 into 4,5-dicyano-1,8-dimethyl-2,7-diaza-3,6,9,10-tetraoxatetracyclo[6.2.1.0^{2,6}.0^{5,7}] undecane 9 in moderate yield. The assigned structure was supported by spectroscopic and other analytical data (see Experimental Section). Thermolysis gave 2,4-pentanedione and intractable material. Neither an epoxide of the olefin 6[19] nor dicyanofuroxan 11[3], an expected fragmentation product, was detected.



Intractable mixtures were obtained from the bisoxaziridine 9 by thermolysis and by further treatment with peroxides. The formation of either a nitrosonitro- 11 or a dinitromaleonitrile 12 was not established. Triphenylphosphine deoxy-

genated the cyclic peroxide 9 into the diazepine 1 in small amounts.

Acknowledgements: Financial support from O.N.R. FD mass spectra from the School of Chemical Sciences, University of Illinois, Urbana, Illinois.

Experimental

Instruments included Perkin Elmer 237B and 521 grating i.r.; Varian A-60 n.m.r.; and Varian MAT 731 FD mass spectrometer. Selected m/e(70 eV) values and all FD values are reported. Each yield was based on starting material consumed. Elemental analyses were provided by Micro-Tech Laboratories, Skokie, Illinois.

Preparation of the diazepine 1a: A condensation between diaminomaleonitrile and 2,4-pentanedione gave the diazepine, mp 202-204°C (dec); ^{1} ^{13}Cnmr ($(CD_3)_2SO$): δ 26.2 (CH_3), 49.4(CH_2), 115.3(CN), 122.9(C=C) and 158.3(C=N).

Preparation of the cyclic peroxide 2a: To an ice-cooled stirred suspension of the diazepine 1a (8.0g,46.5 mmoles) in methanol(100 ml) was added a few drops of 1 N sodium hydroxide solution followed by dropwise addition of 90 percent hydrogen peroxide (2.8 ml,100 mmoles). The mixture was stirred until the disappearance (about 3 h) of the diazepine 1a (tlc) left a clear yellow solution. The reaction mixture was concentrated at a temperature below 45°C until a crystalline solid 2a appeared. Dilution with ice-water brought further separation of the peroxide 2a as a light yellow solid which was filtered and dried at room temperature, 7.2g(75%), mp 125-6°C(dec) (ethyl acetate and hexane); ir(KBr):3333(NH), 2222(CN), 1634(C=C) cm^{-1}; ^{1}H-nmr (acetone-d_6): δ 1.68 (s), 2.5-3.2 (m) and 6.57 (br), (D_2O): δ 1.68 (s,6H), and 2.53-3.05 (2H, AB quartet, J = 12 Hz); ^{13}C-nmr (acetone-d_6): δ 23.90 (CH_3), 57.57 (CH_2), 94.40 (C-O). 105.49 (C=C) and 116.95 (CN); m/e (70 eV) (%):206(6) (M^+), 100(100), 95(100); m/e(FD): 206(100)M^+; found: C, 52.08; H, 4.85; N, 27.03 %; $C_9H_{10}N_4O_2$ requires C, 52.42; H, 4.85; N, 27.18 %.

Efficient cooling during slow addition of the hydrogen peroxide to the diazepine 1a controlled an otherwise violent reaction and prevented the formation of oxamide. Both higher temperatures and complete evaporation of the solvent in the rotary evaporator led to product decomposition. The peroxide 2a was stable on refrigeration but exposure to the atmosphere or storage at room temperature brought about blackening and apparent polymerization. The peroxide was also produced (80%) in acetonitrile at room temperature for 17 hours. In methanol the

formation of oxamide predominated on prolonged reaction time, with or without added pyridine. After the peroxide 2a in methanol was stirred at room temperature for 90 hours, 2,4-pentanedione but not the peroxide 2a was detected (tlc).

Treatment of the peroxide 2a (100 mg, 0.5 mmol) with hydrogen peroxide (90%,0.8 ml) in methanol at room temperature for 20 hours gave oxamide (47%), 2,4-pentanedione (tlc) and the odor of an isocyanide.

To a solution of triphenylphosphine (700 mg, 2.7 mmoles) in benzene (25 ml) the peroxide 2a (500 mg, 2.5mmoles) was added and the mixture stirred for 17 hours. The separated colorless solid was filtered and washed with benzene and was identified (tlc) as the diazepine 1a (300 mg, 72 %), mp and mixture mp 201-3°C.

Preparation of the bisimine 5: To a stirred suspension of iodobenzenediacetate (4.0 g, 12 mmoles) in benzene (100 ml) the cyclic peroxide 2a (2.0 g, 10 mmoles) was added in portions. The reaction mixture was stirred for 64 hours at room temperature and filtered to remove unidentified solid material (90 mg). The filtrate on concentration and addition of hexane gave the bisimine 5 as a light yellow solid, 1.7 g(85 %), mp 161-3°C (ethyl acetate and hexane), dec around 170°C; ir ($CHCl_3$): 2230 (CN), 1628, 1588 cm^{-1}; ^{1}H-nmr($CDCl_3$-acetone-d_6): δ 1.86(s, 6H, $2CH_3$) and 3.20(s, 2H, CH_2); ^{13}C-nmr($CDCl_3$-DMSO-d_6): 23.24 (CH_3), 50.93 (CH_2), 96.58 (C-O), 114.75 (CN), and 136.62 ppm (C=N); m/e (70 eV) (%); 172(52), 163(7), 131(100), 100(15), 91(85); m/e (FD): 204(100)M^+, 172(90), 163(10) and 100(10); found: C, 52.67; H, 4.05; N, 26.86; O, 16.69; $C_9H_8N_4O_2$ requires: C, 52.94; H, 3.95; N, 27.44; O, 15.67 %.

Preparation of the bisepoxide 9: To a stirred suspension of m-chloroperbenzoic acid (2.2 g, 12.8 mmoles) in acetone (100 ml) the bisimine 5 (980 mg, 4.8 mmoles) was added in portions at room temperature. The reaction mixture was stirred for 3 hours and concentrated. The residue was dissolved in ethyl acetate, washed with aqueous sodium bicarbonate solution and dried ($MgSO_4$). Removal of solvent furnished a solid (1.0 g) which showed three tlc spots. Chromatography over a silica gel column (25 x 2 cm) gave di-(m-chlorobenzoyl)peroxide, mp 118-120°C(dec)(lit.[11] mp 122-3°C), 80 mg, also obtained from a sample of MCPBA on elution with a mixture of chloroform and hexane (1:9). Elution with a 3:7 mixture of chloroform and hexane gave the bisoxaziridine 9 (200 mg, 17.7 %) as a colorless solid, mp 117-8°C(chloroform-hexane); 140 145°C (dec); ir (CH_2Cl_2): 2245 cm^{-1}

(CN); ^{1}H-nmr ($CDCl_3$); δ 1.72 (s,3H), 1.83 (s,3H) and 2.50-3.15 (AB quartet, 2H, J = 15 Hz); ^{13}C-nmr ($CDCl_3$): δ 20.11 (CH_3), 25.07 (CH_3), 49.31 (CH_2); 74.97 (C-CN) 97.17 (CH_2CO) and 101.88 (CN); m/e (70 eV) (%): 204(1), 100(100); m/e (FD): 237 (100)(MH^+), 186(23), 100(85); found: C, 45.79; H, 3.40; N, 23.85; $C_9H_8N_4O_4$ requires C, 45.77; H, 3.41; N, 23.72%.

Elution with chloroform gave a semisolid (360 mg) which on trituration with a mixture of ethyl acetate and hexane gave a colorless solid, mp 147-9°C (dec) (chloroform-hexane); found: C, 45.17 and 45.22; H, 4.23 and 4.26; N, 19.88 and 19.65; $C_9H_8N_2O_4$ requires: C, 45.50; H, 4.30; N, 19.90 %. It has tentatively been identified as 4-cyano-1,8-dimethyl-2,7-diaza-3,6,9,10-tetraoxatetracyclo[6.2.1. $0^{2,7}$ $0^{5,7}$]undecane, cf. 9 with one cyano group replaced by hydrogen, and will be further investigated.

Preparation of the methanol adduct 8: The bisimine peroxide 5 (100 mg) was dissolved in methanol (5 ml) and a drop of dilute sulfuric acid added. A colorless solid started to separate gradually. After stirring for 17 hours, the reaction mixture was concentrated, diluted with water and filtered to isolate the bis methanol adduct 8 as a colorless solid; 70 mg (52 %); mp 188-190°C (dec) (methanol); ir (KBr): 3330, 2230, 1520, 1495 cm^{-1}; ^{1}H-nmr(DMSO-d_6); δ 3.36 and 3.41 (2 s,6H), 5.6 and 5.7 (2 broad s, 2H, exchanged with D_2O), 2.2-3.0 (AB quartet partly hidden in DMSO peaks, J = 12.5 Hz) and 1.4 (s,6H); m/e (70 eV) (%): 236(18), 235(100), 100(80), 85(100); m/e(FD): 268(100)M^+, 236(10), 235(34) and 98(12); found: C, 49.06; H, 5.95; N, 20.77; $C_{11}H_{16}N_4O_6$ requires C, 49.25; H, 6.01; N, 20.88 %.

A solution of the bisimine 5 (400 mg, 2 mmoles) in benzene (50 ml) was treated with triphenylphosphine (1.05 g, 4 mmoles) added in portions. The reaction mixture turned red-brown. A solid which separated over several hours with stirring was triturated with benzene and ethanol to give the diazepine (tlc) 1a, mp and mixture mp 200-202°C.

†On leave from University of Madras, P.G. Centre, Coimbatore, 641041, India.

References and footnotes.

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OXIDATION AT NITROGEN IN BENZO- BENZODI- AND BENZOTRIFUROXANS

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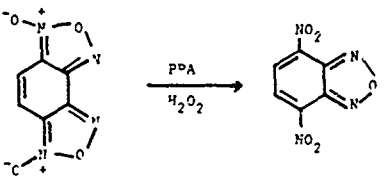
Abstract - Hydrogen peroxide in sulfuric acid oxidized 5-nitrobenzofuroxan into 1,2,4-trinitrobenzene and completed the oxidation of a mixture from benzodifuroxan and hydrogen peroxide in polyphosphoric acid into 1,2,3,4-tetranitrobenzene. The incompletely oxidized mixture also contained 4,7-dinitrobenzofurazan, a terminal oxidation product. Benzotrifuroxan was unreactive toward peroxidation.

In either sulfuric or trifluoroacetic acid hydrogen peroxide rapidly degraded benzodifuroxan 1 but in polyphosphoric acid it smoothly converted the difuroxan 1 into a mixture. Recrystallization brought about partial isolation of 4,7-dinitrobenzofurazan 2. Further treatment of the mixture by oxidation with hydrogen peroxide in sulfuric acid gave 1,2,3,4-tetranitrobenzene 3 and the furazan 2; however the latter was not a precursor to the tetranitrobenzene since it resisted all attempts to bring about oxidation at a furazan nitrogen atom.[1] Similar peroxidation of benzofuroxan into 1,2-dinitrobenzene, 4-nitrobenzofuroxan into 1,2,3-trinitrobenzene and 4,6-dinitrobenzofuroxan into 1,2,3,5-tetranitrobenzene was previously reported.[2] Benzotrifuroxan[3] was quantitatively recovered from attempts at peroxidation into hexanitrobenzene, a recently reported compound.[4]



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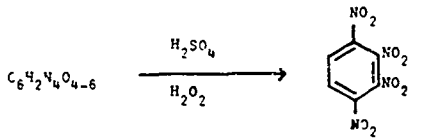

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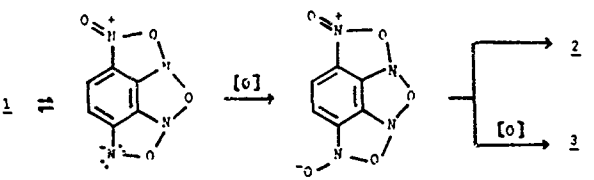
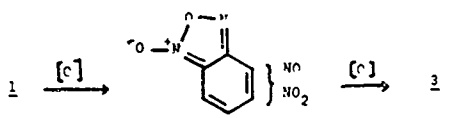
A neighboring group participation 1 → 4 between furoxan moieties and cleavage of two oxygen bridges in the intermediate 5 can account for a terminal monoxidation 1 → 2. On the other hand differentiation between intermediate 5 and an isomeric nitronitrosobenzofuroxan 6 for the oxidation 1 → 3 cannot be made at this time.





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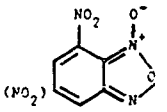
An intermediate neighboring group participation between a furoxan moiety and a 4-nitro substituent with or without the intermediacy of nitronitrosobenzenes 8, may have occurred in the oxidations of 4-nitro- and 4,6-dinitrobenzofuroxans 7 into the corresponding polynitrobenzenes 9[2,3] We now report an efficient oxidation of 5-nitrobenzofuroxan 10 by hydrogen peroxide in sulfuric acid into 1,2,4-trinitrobenzene 12. This example presumably proceeds via a dinitronitrosobenzene 11 intermediate.



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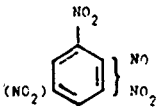

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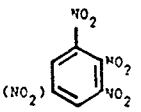

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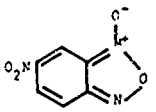

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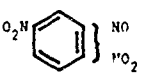

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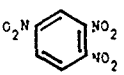

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The identification of 4,7-dinitrobenzofurazan 2 was consistent with a single nmr ^1H signal for two equivalent hydrogen atoms, ir absorption for the nitro groups, molecular weight (ms), elemental analyses and resistance to oxidation by Caro's acid. The structure of 1,2,3,4-tetranitrobenzene 3 was supported by a single nmr ^1H signal, ir absorption for the nitro groups, molecular weight (ms), elemental analyses, a mixture melting point and the same R_f value obtained from a known sample.[5]

Acknowledgment: Financial support was received from O. N. R. Certain n.m.r. spectra were obtained from a Bruker 270MH instrument at the University of Chicago, Chicago, Illinois.

Experimental

Instruments included Perkin Elmer 237B, 283 and 521 grating i.r.; Varian A-60 and Bruker 270 n.m.r.; and an AEC Scientific limited MS 30 (70 ev, source temperature 120-150°C).

Hydrogen peroxide (90%, 4ml)[6] was added over a period of four hours to a solution of benzodifuroxan (0.22 g, 1.13 mmol) in polyphosphoric acid (10 ml).[8] After stirring at room temperature for two days,[9] ice water was added, and the products extracted into methylene chloride which was dried (magnesium sulfate), filtered and evaporated to dryness to give a mixture of yellow solids, 0.09 g. Recrystallization from ethyl acetate gave 4,7-dinitrobenzofurazan 2, 0.03 g,

mp 187-189°C; nmr(ethyl acetate): δ 8.6(s); ir(KBr); 3045,1550,1530 (NO_2),1480, 1380 and 1340 cm^{-1} (NO); m/e(70eV) (%); 210(100) M^+; calcd for $C_6H_2N_4O_5$: C, 34.28;H, 0.95; N, 26.67%; mw 210;, found: C, 34.16; H, 0.93; N, 26.42%.

The mixture of yellow solids, 0.09 g, in sulfuric acid (98%, 20 ml) was treated with hydrogen peroxide (90%, 2 ml) added slowly over a period of two hours. The reaction mixture was stirred at room temperature for three days and worked up in the manner described above. Removal of methylene chloride left a yellow solid. 1,2,3,4-Tetranitrobenzene 3 was extracted by, and then recrystallized from, carbon tetrachloride as a yellow solid, 0.03 g (12%), mp 108-109°C Elution from silica gel by a mixture of methylene chloride and carbon tetrachloride (3:2) gave a pure sample, mp 115-116°C, mixture mp 114-116°C with an authentic sample;[4] nmr ($CDCl_3$): δ 8.50; ir (KBr): 1550 and 1350 cm^{-1} (NO_2); calcd for $C_6H_2N_4O_8$: C, 27.92; H, 0.78; N, 21.71; found: C, 28.79; O, 0.53; N, 21.50; R_f 0.3 from a tlc silica gel plate by a mixture (3:2) of methylene chloride and carbon tetrachloride.

The portion insoluble in carbon tetrachloride gave the furazan 2 0.05 g, mp 187-189°C after recrystallization from ethyl acetate (combined yield 21 %).

To a solution of 5-nitrobenzofuroxan 9[10] (0.40g, 2.2 mmol) in sulfuric acid (98%, 30ml), hydrogen peroxide (90%, 2.0 ml, 82 mmol) was added dropwise at 0°C over a period of 4 hours, stirred at 25°C for 2 days, diluted with ice-water and extracted with metheylene chloride. The extract was dried over magnesium sulfate, filtered and concentrated to give 1,2,4-trinitrobenzene 11 (0.38g, 1.8 mmol, 80% yield), m.p. 58-60°C[11] after recrystallization from chloroform; nmr ($CDCl_3$): δ 8.86 (s, 1H), 8.69-8.68(d,1H), 8.15-8.12(d,1H); ir(KBr): 1540 and 1350 cm^{-1} (NO_2).

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5. A. J. Boulton and A. K. Katritzky, Proc. Chem. Soc., 1964, 299 assumed a similar neighboring group participation to account for the degenerate isomerization of 4-nitrobenzofuroxan.

6. Hydrogen peroxide(90 %) must be handled as a dangerous reagent. The compounds 1 - 6 are potentially explosive.

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8. When polyphosphoric acid was replaced by either sulfuric or trifluoroacetic acid extensive degradation occurred with the evolution of brown fumes of nitrogen oxides.

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Oxidation of Nitrobenzofuroxans

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Summary Monoperoxosulphuric acid oxidized 4-nitrobenzofuroxan into 1,2,3-trinitrobenzene (80%) and 4,6-dinitrobenzofuroxan into 1,2,3,5-tetranitrobenzene (100%)

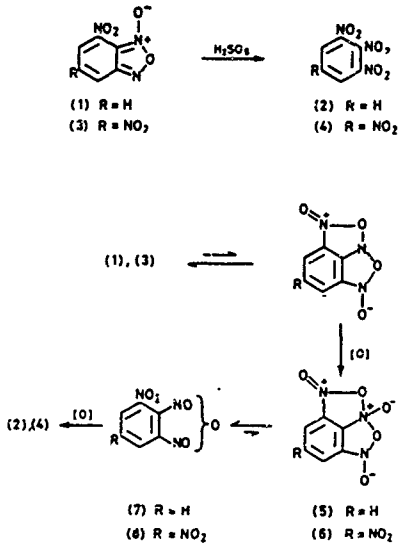
Oxidation of 4-nitro- (1)[1] and 4,6-dinitro-benzofuroxan (3)[1] into 1,2,3-trinitrobenzene (2), m p 120—122 °C,[2] (80%) and 1,2,3,5-tetranitrobenzene (4), m p 129—130 °C,[3] (99%) extends the only previous oxidation of a furoxan into a dinitro-compound,[4] and in combination with the nitration of benzofuroxan,[1] provides a preparative route to vicinal trisubstitution

The highly efficient oxidations,† (1) → (2)‡ and (3) → (4)[5] were brought about by a large excess (> 50 molar) of hydrogen peroxide (90%) in sulphuric acid (98%) at 25 °C for 2 days When polyphosphoric acid replaced sulphuric acid the yield of the tetranitrobenzene (4) was moderate (44%) but in mixtures of the two acids the yield increased with increasing sulphuric acid content and was quantitative with 80% sulphuric acid alone

Trifluoroperoxyacetic acid by itself or mixed with concentrated nitric acid failed to react with 4,6-dinitrobenzofuroxan but a mixture of trifluoroacetic and nitric acids and hydrogen peroxide in polyphosphoric acid transformed the furoxan (3) into the tetranitrobenzene (4) in trace amounts

Benzofuroxan was oxidized into *o*-dinitrobenzene (20%) by both trifluoroperoxyacetic[6] and monoperoxosulphuric acid (there was extensive degradation); however, the furoxans (1) and (3) resisted oxidation by trifluoroperoxyacetic acid and were recovered. Diminished attraction between the furoxan ring and electrophilic peroxide is the expected result of electron withdrawal into the nitro-substituent(s); however, this could be partially balanced by neighbouring group participation by the 4-nitro-substituent (see Scheme), an effect previously assumed to be operative in the degenerate rearrangement of 4-nitrobenzofuroxan and similar rearrangements.[4] It was assumed that the oxygen atoms were introduced in separate steps Isomerization during or after the first stage of the oxidation of the furoxans (1) or (3) into the nitroso-compounds (7) or (8) was not detected, however, we assume that a facile oxidation of a nitrosoarene into a nitroarene is one step in the reactions

Financial support was received from the Office of Naval Research.



(1) R = H
(3) R = NO_2
(2) R = H
(4) R = NO_2
(7) R = H
(5) R = H
(8) R = NO_2
(6) R = NO_2

Scheme

(*Received, 3rd November* 1980, *Com* 1175)

† *CAUTION* 90% hydrogen peroxide is dangerous Each reaction was repeatedly carried out on a scale (1—2 mmol) which called for less than 3 ml (160 mmol) of 90% hydrogen peroxide without mishap

‡ Compound (2), δ (EtOAc) 8·60—8·75 (d, 2H) and 9·05—9·30 (t, 1H), *m/e* (70 ev) 213 (M^+), compound (4) δ ($CDCl_3$) 9·3 (s), *m/e* (70 ev): 258 (M^+).

[1] A. G Green and F M Rowe *J Chem Soc*, 1913, 103, 2023

[2] L. I Khmel'nitskii, T S Novikova, and S S Novikov, *Izv Akad Nauk SSSR, Otd Khim Nauk*, 1962 517 (*Chem Abstr*, 1962, 57 14979b) reported the oxidation of 2,6-dinitroaniline by hydrogen peroxide (96%) in trifluoroacetic acid into 1,2,3-trinitrobenzene (2), m p. 122 °C

[3] A T Nielsen, R L. Atkins and W P Norris, *J Org Chem*, 1979, 44, 1181 oxidized picramide by hydrogen peroxide (96%) in sulphuric acid (100%) into the tetranitrobenzene (4), m p 127—129 °C

[4] J H Boyer and S E Ellzey, *J Org Chem* 1959, 24 2038 The reported procedures were adapted to the present work.

[5] R Nietzki and R Dietschy *Ber*, 1901, 34, 55, W Will *ibid*, 1914, 47, 704, 983 The oxidation of (3) into (4) by nitric acid reported in 1901 was refuted in 1914

[6] A. J. Boulton and A R. Katritzky, *Proc Chem Soc*, 1962, 257

THE AMBIPHILIC FUROXAN RING. BENZOFUROXAN OXIDATION BY PERACID AND REDUCTION BY COPPER.[1]

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Abstract.

Monopersulfuric acid, trifluoroperacetic acid and hydrogen peroxide in polyphosphoric acid, or with selenium dioxide in t-butyl alcohol, or in tetramethylene sulfone have each oxidized benzofuroxan into o-dinitrobenzene. Monopersulfuric acid oxidized 4-nitrobenzofuroxan into 1,2,3,5-tetranitrobenzene(99 %); hydrogen peroxide in polyphosphoric acid was moderately efficient for the latter oxidation. Copper in acidified ethanol transformed 4,6-dinitrobenzofuroxan into picramide quantitatively.

Introduction.

A. General. Although 1a ⇄ 1b abbreviated to 1a or 1b is the accepted symbol for benzofuroxan,[2,3]

it tends to disguise the disposition toward electron donation and acceptance shown by the heterocyclic ring.

Dinitrogen tetroxide, manganese dioxide in acetic acid, and nitric acid have oxidized oximes into nitronic acids 2 or the tautomeric nitro compounds,[4,5] but failed to oxidize the heterocyclic ring in the furoxan 1, an oxime-nitronic acid anhydride. Peracetic and perbenzoic acids have fragmented trialkylhydroxylamines, presumably via initial oxidation into a hydroxylamine-N-oxide 3,[6] but failed to oxidize the heterocyclic ring in the furoxan 1, a latent hydroxylamine by virtue of 1c ↔ 1d ↔ 1a ↔ 1b.

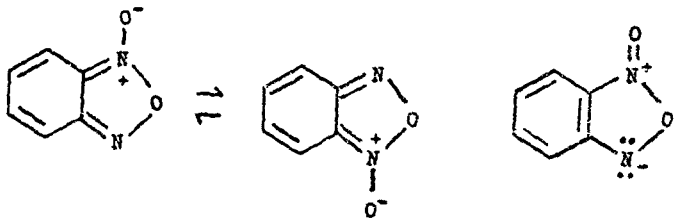
Resistance toward N-oxidation is also characteristic of isoxazoles 4, isoxazolines 5, furazans 6, and presumably other oxime esters, both cyclic and linear;[7] however, the contrary is implied by the extended principle of the α-effect.[8]

B. Electron Donation. On the other hand, trifluoroperoxyacetic acid was successful, where performic and peracetic acids were not,[9] in oxidizing benzofuroxan into o-dinitrobenzene 7 and 5-methylbenzofuroxan into 3,4,-dinitrotoluene; but the efficiencies (15-20 %) were in marked contrast with the similar oxidation of p-di-

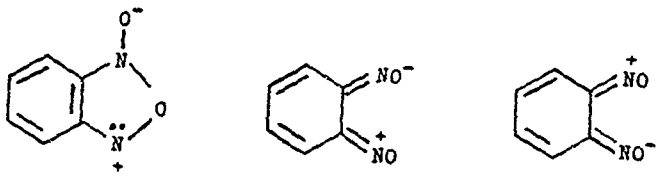
nitrosobenzene into p-dinitrobenzene (92 %).[10] Extensive degradation of naphtho- and phenanthrofuroxan and 5-chloro-6-methoxybenzofuroxan, attributable to oxidation initiated at carbon atoms, occurred without affording detectable amounts of nitro compounds.[10]

An older,[11] discredited,[12] claim for oxidation of oximes by monopersulfuric acid (Caro's acid) has now been indirectly supported by an oxidation of benzofuroxan by hydrogen peroxide in sulfuric acid.

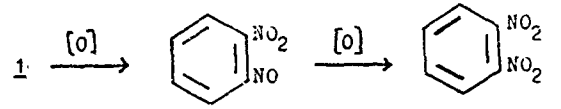
Unsymmetrical diarylfuroxans 8 were fragmented and oxidized into aromatic acids when treated with ozone. A preferential electrophilic attack by ozone on the N-oxide side of the heterocycle was invoked.[13,14]



1a ⇌ 1b 1c



1d 1e 1f



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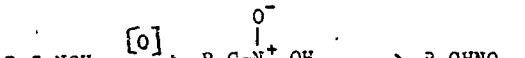

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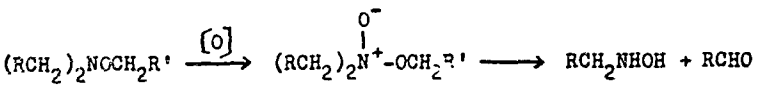

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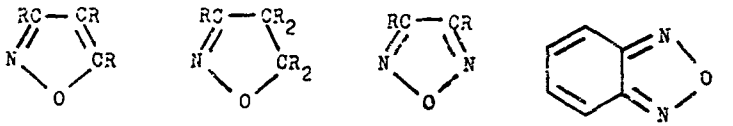
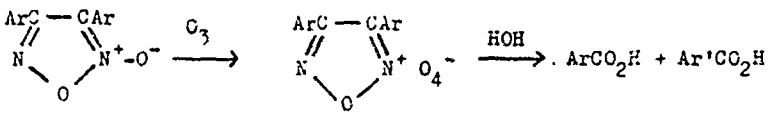


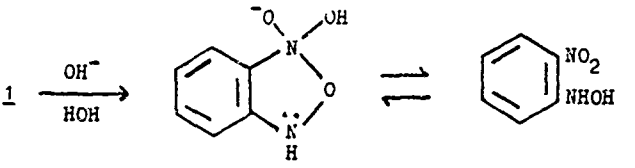
4 5 6 16



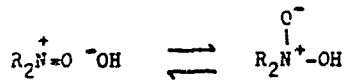
8

C. Electron Acceptance. An addition of water to benzofuroxan (an anhydride) [illegible] is unknown; however, the adduct 9 ≠ 10 is related to a nitrosonium hydroxide 11a ≠ 11b, recently reported.[15] Electron acceptance at a furoxan nitrogen atom, related to the re-

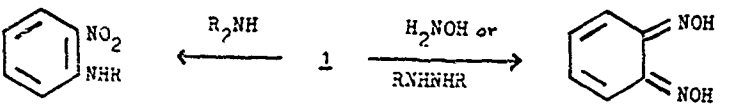
quirement for the formation of the adduct 9 has been demonstrated in the transformation of a benzofuroxan into an o-nitrophenylhydrazine by a secondary amine,[16] and in the reduction of a benzofuroxan into a dioxine by either hydroxylamine,[17] a hydrazine[18] or copper.[2b]



9 10



11a 11b



Results and Discussion. o-Dinitrobenzene 7 was obtained from benzofuroxan 1 and hydrogen peroxide (90 %) in polyphosphoric or sulfuric(80 %) acids or in tetramethylene sulfone, and with hydrogen peroxide (90 %) and selenium dioxide in t-butyl alcohol. Although protonation of benzofuroxan, pKa -8.3,[19] in sulfuric acid (98 %, pKa -10.3; 80 %, pKa -7.5)[20] can

be assumed, its assistance, if any, to the oxidation was not determined. Just as the location of protonation has not been established,[21] it is not possible to differentiate between peroxide attack at a nitrogen or an oxygen atom in the oxidation of a benzofuroxan into an o-dinitrobenzene. It was assumed that the formation of new carbon-oxygen bonds by either electrophilic or nucleophilic attack initiated extensive degradation.

In a mixture of nitric acid and hydrogen peroxide benzofuroxan afforded 4-nitro- 12 and 4,6-dinitrobenzofuroxan 14 but neither o-dinitrobenzene 7 nor nitrated derivatives, e.g., 13 and 15, were detected. Apparently an electrophilic attack on the heterocyclic portion of the molecule by a peroxide or other oxidant was not competitive with nitration and the peroxides present did not attack the furoxan ring in the nitro compounds 12 and 14. Degradation was attributed to oxidation at carbon atoms in compounds 1, 12 and/or 14.

Benzofurazan 16 and diphenylfuroxan 8 (Ar = Ar' = C_6H_5) were each unreactive toward monopersulfuric acid (the most effective peroxide reagent) and other peroxides.

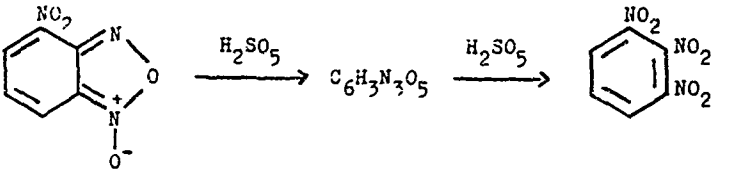
With an absence of extensive peroxidative degradation, 4-nitro- 12 and 4,6-dinitrobenzofuroxan 14

gave 1,2,3-trinitro- 13 and 1,2,3,5-tetranitrobenzene 15 in excellent to quantitative yields when treated with hydrogen peroxide(90 %) in concentrated sulfuric acid(98 %). These are attractive preparative procedures however the danger associated with hydrogen peroxide (90 %) must be recognized. An inability of trifluoro-peroxyacetic acid to oxidize either furoxan, 12 or 14, is partially attributable to a deactivation of the furoxan ring nitrogen and oxygen atoms by the nitro substituent(s). The superior performance of mono-persulfuric acid was revealed by the investigations on 4,6-dinitrobenzofuroxan in mixtures of sulfuric acid and polyphosphoric acids. When only poly-phosphoric acid was present the yield of the tetra-nitrobenzene 15 was 44 %; when only sulfuric acid was present the yield was 100 % (Table I). Oxidative degradation may partially account for the deficiency in mass balance for reactions in polyphosphoric acid. The greater reactivity of the mononitrofuroxan 12 was shown in a series of experiments in which mixtures of 12 and the dinitrofuroxan 14 competed for oxidation. A large molar excess (40 to 80) of peroxide was required for satisfactory efficiency. (Table II).

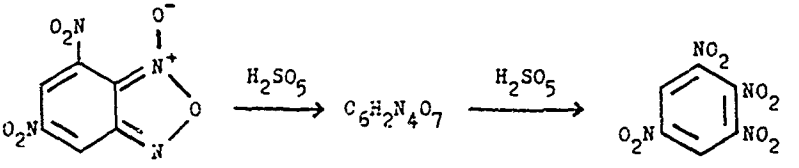
TABLE I.

TABLE II.

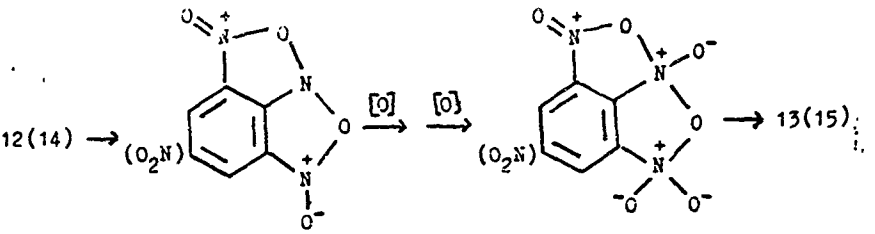
Two stages in the oxidation of benzofuroxan into a polynitro compound via a nitrosonitro intermediate, e.g., 17, were probably involved. A retardation at either stage may reflect deactivation by electron withdrawal into (the) nitro substituent(s) in compounds 12 and 14.[22] On the other hand there may be a balancing activation by a neighboring group participation of the 4-nitro substitutent, cf. 18 and 19.[23] Further insight will be sought by investigating the oxidation of 5-nitrobenzofuroxan into 1,2,4-trinitrobenzene.



12 13

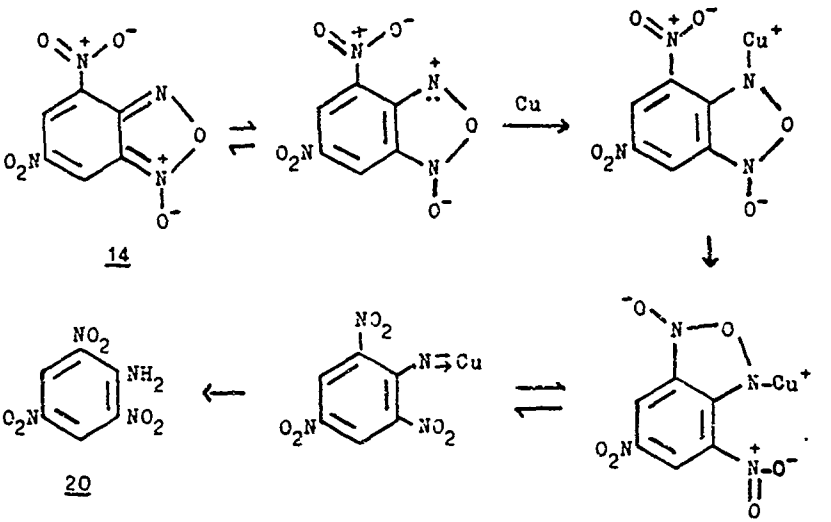


14 15



18 19

A highly specific quantitative reduction of 4,6-dinitrobenzofuroxan 14 into picramide 20 without the formation of a detectable amount of an isomeric amine by treatment with copper bronze in ethanol is now reported.[2b] In a transfer of an electron from copper to the heterocyclic ring, a control in the selection of the nitrogen atom to be bound to copper is provided by electronic and steric factors associated with the 4-nitro substituent as shown in the scheme.



14 20

Experimental Section. The infrared spectra were recorded on a Perkin Elmer grating infrared spectrophotometer model 237B or 521. NMR spectra were obtained on a Varian A-60 or T-60 spectrometer with TMS as an internal standard. Mass spectra were recorded on AEI Scientific Apparatus Limited MS 30 double beam mass spectrometer at 70 ev with source temperature 120-150°C. Elemental analyses were carried out by Micro Tech Laboratories, Inc., Skokie, Illinois.

The following compounds are commercially available: benzofuroxan, mp 69-71°C, hydrogen peroxide, 90 %, d = 1.54; o-dinitrobenzene, mp 117-118°C; selenium dioxide, mp 315°C; tetramethylene sulfone, mp 27°C; 4-chloro-2-nitroaniline, mp 115-116°C; m-dichlorobenzene, bp 172-173°C; benzil, mp 94-95°C.

The following compounds were prepared according to the literature: 4,6-dinitrobenzofuroxan, mp 171-172°C;[24] 4-nitrobenzofuroxan, mp 142-143°C;[24] polyphosphoric acid;[25] benzofurazan, mp 55-56°C;[26] diphenylfuroxan, mp 117-118°C.[27]

Except where otherwise specified a product yield was based on recovered starting material.

Oxidation of benzofuroxan in polyphosphoric acid. To a solution of benzofuroxan (1.36 g, 10 mmol) in

polyphosphoric acid (30 ml), hydrogen peroxide(90 %, 3 ml, 123 mmol) was added dropwise at 0°C over a period of 4 h, and stirred for 18 h at room temperature, and 24 h at 60-65°C. The reaction mixture was diluted with ice water and extracted with methylene chloride. The extracts were dried with magnesium sulfate, filtered, and concentrated to dryness to give o-dinitrobenzene, mp 115-117°C[10] (0.41 g, 2.5 mmol, 25 %).

A similar treatment in sulfuric acid(80 %, 20 ml) and hydrogen peroxide(90 %, 1 ml, 41 mmol) afforded 0.22 g(13 %) of o-dinitrobenzene, mp 117-118°, from benzofuroxan (1.36 g, 10 mmol).

Nitration of benzofuroxan in nitric acid(70 %), free of nitrous acid, and hydrogen peroxide(90 %) at 0°C for 6 h and stirring for 3 days at 25°C afforded 4-nitrobenzofuroxan, mp 142-143°C (40 %) and 4,6-dinitrobenzofuroxan, mp 171-172°C (21 %). An unidentified pale yellow solid, mp 126-130°C, soluble in water and in methanol(60 %) was also obtained.

Benzofuroxan gave o-dinitrobenzene(17 %) when oxidized by hydrogen peroxide(90 %) in tetramethylene sulfone or by hydrogen peroxide(90 %) and selenium dioxide in t-butyl alcohol. In 16 and 56 % amounts, benzo-

furoxan was respectively recovered.

Oxidation of 4,6-dinitrobenzofuroxan in sulfuric acid. To a solution of 4,6-dinitrobenzofuroxan (0.50 g, 2.2 mmol) in sulfuric acid(98 %, 30 ml), hydrogen peroxide(90 %, 4 ml, 164 mmol) was added dropwise at 0°C over a period of 4 h and stirred for 3 days at room temperature. Methylene chloride extractions from the reaction mixture diluted with ice water were dried ($MgSO_4$), filtered and concentrated to dryness to give a yellow solid mixture, 0.56 g. Nmr analysis showed the presence of 1,2,3,5-tetranitrobenzene, 0.51 g (99 %) and 0.05 g (10%) of 4,6-dinitrobenzofuroxan. Recrystallization from chlorofo gave 1,2,3,5-tetranitrobenzofuroxan, mp 126-127°C,[28] nmr($CDCl_3$): δ 9.3(s), m/e 70ev: 258(M^+).

A similar treatment transformed 4-nitrobenzofuroxan into 1,2,3-trinitrobenzene, mp 120-122°C[29] (80 %) after recrystallization of the residue obtained by evaporating to dryness a methylene chloride solution; nmr(ethyl acetate): δ 8.60-8.75(d,2 H) and 8.05-8.30 (t,1 H); m/e (70 ev): 213(M^+).

Oxidation of 4,6-dinitrobenzofuroxan in mixtures of sulfuric and polyphosphoric acids. To a solution of 4,6-dinitrobenzofuroxan (0.50 g. 2.2 mmol) in a mixture

of sulfuric(98 %) and polyphosphoric acids (30 ml), hydrogen peroxide (90 %, 3 ml, 123 mmol) was added dropwise at 0°C over a period of 4 h, and stirred for 3 days at room temperature. Methylene chloride extractions, obtained from the reaction mixture diluted with ice water, were dried with magnesium sulfate, filtered, and concentrated to dryness to give a yellow solid mixture. Analysis by nmr quantitatively established the presence of 1,2,3,5-tetranitrobenzene and starting material. The results are presented in Table I.

Reduction of 4,6-dinitrobenzofuroxan 14 by copper.[30]

To the furoxan (1.0 g, 4.4. mmol) in methanol (100 ml) copper (0.422 g, 67 mmol), or copper bronze powder, and hydrochloric acid(37 %, 1 ml) were added. The mixture was heated to reflux for 22 h and filtered. The filtrate was combined with an acetone wash of the precipitate and concentrated by evaporation and the residue isolated by chromatography from an alumina column or by recrystallization to give picramide, mp 188-190°C,[31] 0.88 g(87 %). When the reaction was run in ethanol the yield was 80 %.

Acknowledgment: Partial financial support was received from the Office of Naval Research.

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TABLE I

Oxidation of 4,6-Dinitrobenzofuroxan 14 in mixtures of sulfuric and polyphosphoric acids (PPA) and hydrogen peroxide.[a]

Run number	Volume, %		Product mixture, g	Recovered 13, %[d]	Product 17 yield, %[d]
	H_2SO_4[b]	PPA[c]			
1	0	100	0.45	83	44
2	10	90	0.48	90	50
3	30	70	0.47	90	55
4	50	50	0.47	87	50
5	80	20	0.47	52	76
6	90	10	0.53	40	97
7	100	0	0.54	33	100

[a]In each run there was 0.5 g (2.8 mmol) of the furoxan 14 and 3.0 ml (123 mmol) of H_2O_2 (90 %) in 30 ml of acid or acid mixture. [b]98 %. [c]ref. 25. [d]The composition of each product mixture in ethyl acetate was determined by an nmr analysis with authentic samples as standards. The yield of nitro compound 15 was based on converted starting material.

TABLE II

Oxidation of Equimolar[a] Mixtures of 4-Nitrobenzofuroxan 12 and 4,6-Dinitrobenzofuroxan 14 in Monopersulfuric Acid[b]

Run number	Hydrogen Peroxide, ml	Time, days	Recovered furoxans (%)[c]	Nitro compounds (%)[c]
1	2[d]	1	12 (0)	13 (80)[e]
			14 (73)	15 (27)[f]
2	2[d]	2	12 (0)	13 (78)[e]
			14 (70)	15 (30)[f]
3	1[g]	1	12 (trace)	13 (75)[e]
			14 (80)	15 (20)[f]
4	1[g]	2	12 (trace)	13 (78)[e]
			14 (72)	15 (28)[f]

[a] 2.2 mmol of 12 and of 14. [b] 30 ml H_2SO_4 (98 %). [c] Each mixture of furoxans and nitro compounds was quantitatively analyzed by nmr (ethyl acetate) with authentic compounds as standards. Yields are based on 2.2 mmol of starting material. [d] 82 mmol. [e] Degradation of 12 assumed. [f] Quantitative yield based on recovered starting material. [g] 41 mmol.

DICYANOFUROXAN AND HYDRAZINE OR HYDROXYLAMINE

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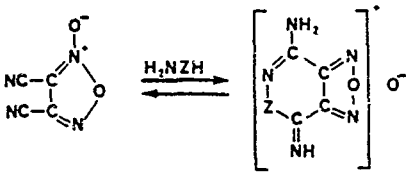
Chicago Circle Campus, Chicago, Illinois 60680 U.S.A.

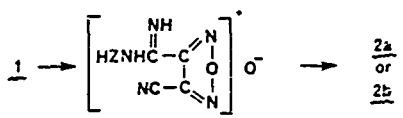
Abstract - Dicyanofuroxan combined with hydrazine to produce 1,4-diamino[4,5-c]pyridazinofuroxan (or an imine tautomer 2a) and with hydroxylamine to produce the imine 2b of 1-oxo-4-amino [4,5-c]oxazinofuroxan; mild thermolysis of the latter adduct gave 3(4)-cyano-4(3)-carbamoyl furoxan 8.

The explosive nature of a mixture[1] of dicyanofuroxan (DCF) 1 and hydrazine may have precluded further investigations on the chemical properties of the system. A reaction, not necessarily important in the explosion process, has been found to occur near 0°C and to provide an efficient preparation of 1,4-diamino[4,5-c]pyridazinofuroxan 2a.[2,3] A similar reaction with hydroxylamine gave the imine 2b of 1-oxo-4-amino[4,5-c]oxazinofuroxan, also in good yield.[3,4]

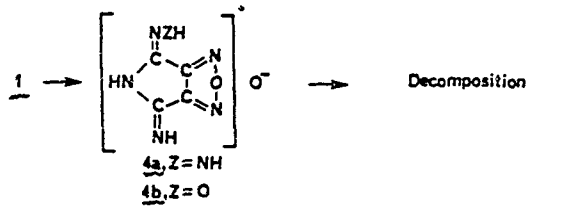


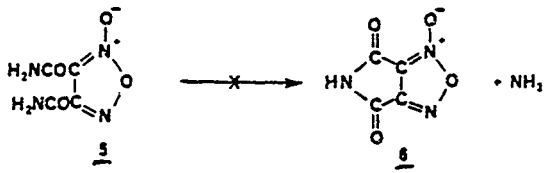
1 2

An amidrazone 3a and an amidoxime 3b were assumed but undetected initial intermediates capable of cyclizing directly into the appropriate product 2a,b. There was no evidence for an alternative cyclization into a pyrrolinofuroxan 4,[5] a molecule subject to the characteristic strain of a 5-5-bicyclic system fused through planar (sp^2) atoms.[6,7] This factor presumably accounted for the failure to obtain a bicyclic imide 6 on heating the diamide 5 of furoxandicarboxylic acid.



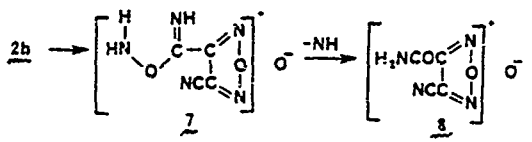
3a, Z = NH
3b, Z = O

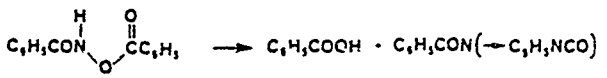




A preference shown by each reagent to react at cyano substituents rather than at dipole centers in the furoxan rings in compounds 1, 2, and 3 is consistent with the inability of other monocyclic furoxans to be reactive toward hydrazines and hydroxylamines. In contrast benzofuroxans have been reduced to dioximes of o-benzoquinones by substituted hydrazines[9] and by hydroxylamine,[7] and to give o-nitroaryl hydrazines on treatment with certain amines.[10]

Moderate heat transformed the oxazinofurcxan 2b into 4(5)-cyano-5(4)-carbamoylfuroxan 3. This rearrangement and elimination can be attributed to an initial tautomerization of 2b into an O-imidoylhdroxylamine 7 a rarely encountered type of molecule. Its ability to undergo thermal elimination of imidogan parallels the loss of benzoyl nitrene from O,N-dibenzoyl hydroxylamine.[11]





Experimental Section

To dicyanofuroxan[12] 1 (1.0 g, 8.0 mmole) in dimethylformamide (DMF) (30 ml) at 0°C hydrazine hydrate (85% 0.8 g, 16 mmole) in DMF (5 ml) was added dropwise over 0.5 hour with stirring which was then continued for 2 hours. Crushed ice was added, the aqueous solution was extracted with ether (200 ml) and the organic layer was washed with cold water (3 x 100 ml). The residue after removal of the ether recrystallized from a mixture of ethyl acetate and hexane as the furoxan 2a, a yellow solid, 67% mp 118-119°C (dec); satisfactory analysis for C, H and N; (KBr): 3460 (m), 3370 (m) and 1600 cm^{-1}(s); nmr($(CD_3)_2CO$): 56.4 (broad singlet, exchanged with (D_2O); m/e (70 eV)(%): 168(100) M^+, 152(5), 151(5), 139(70), 138(15) and 108(90); ^{13}C nmr (DMSO-d_6): 96.64, 107.33, 132.35 and 151.42 ppm.[13]

The substitution of a molar equivalent of hydroxylamine for hydrazine, and methylene chloride for ether in extraction afforded the furoxan 2b as a colorless solid, 78%, mp 143-144°C (dec); satisfactory analysis for C, H and N; ir(KBr): 3470 (m), 3360 (m) and 1610 cm^{-1}(s); nmr ($(CD_3)_2CO$):65.9 (exchangeable with D O); m/e (70 eV)(%): 169(5) M^+, 168(100), (153(5), 138(10), 109(90); ^{13}C nmr (DMSO-d_6): 96.60, 107.00, 142.22 and 150.53 ppm.[13]

Heating in a mixture of ethyl acetate and hexane brought about the change 2b → 8. The amide 8 was obtained as a colorless solid, mp 178-179°C (dec);[14] ir(KBr). 3390 (m) 3300 (w), 3220 (m), 2250 (s), 1700 (s), 1620 (s), 1600 (s), 1485 (m), 1375 (m), 1065 (m), 1030 (m) and 840 cm^{-1} (m); nmr ($(CD_3)_2CO$): 67.35 (broad, exchangeable with D_2O; m/e (70 eV)(%): 154(100) M^+, 139(5), 124(50), 112(50), 111(90), 109(30), 95(5) and 92(5); satisfactory analysis for C, H and N.

Acknowledgment. Financial support was received from the Office of Naval Research.

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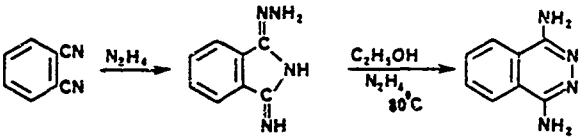

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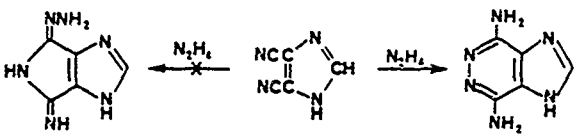

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14. ^{13}C-Chemical shift ranges (ppm) of 102 to 118 and 141 to 167 with an average difference of 42 have been assigned to furoxan carbon atoms. The more upfield value described the furoxan carbon atom closer to the exocyclic oxygen atom[4,15]

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BROMINE OXIDATION OF THE DIPOTASSIUM SALT OF α,α'-DINITROSUCCINONITRILE INTO THE POTASSIUM SALT OF NITROKETOSUCCINONITRILE.

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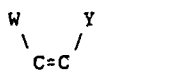
Abstract. The potassium salt 9 of nitroketosuccinonitrile and potassium bromide were produced by bromine oxidation at a nitronate anion in the dipotassium salt of α,α'-dinitrosuccinonitrile.

Introduction. Comparable electronic effects for cyano and nitro groups permit the projection of many of the useful properties of tetracyanoethylene (TCNE)[1] to the other six derivatives in which ethylene is tetrasubstituted by combinations of these two groups. Tetranitroethylene 1, apparently highly reactive,[2] has not been

isolated but has been trapped as its Diels-Alder adducts with anthracene and cyclopentadiene.[3] Tricyanonitro-, trinitrocyano- and 1,1-dicyano-2,2-dinitroethylene and dinitromaleo- 2a and dinitrofumaronitrile 2b remain unknown.



W = X = Y = Z = NO_2 1

W = X = CN, X = Z = NO_2 2a

W = Z = CN, X = Y = NO_2 2b

Unsuccessful attempts to produce olefins 1 or 2 have included (1) coupling from methylene derivatives, e.g., dihalodinitromethane $X_2C(NO_2)_2$,[4,5] dihalonitroacetonitrile $X_2C(NO_2)CN$,[4,6] or nitroacetonitrile, O_2NCH_2CN;[6,7] (2) elimination reactions from hexasubstituted ethanes, e. g., 1,2-dichlorotetranitroethane, $[Cl(O_2N)_2C]_2$;[8] and (3) oxidation at nitrogen in certain derivatives of the NCCN moiety.[9]

Halogen oxidation of dinitronate salts has been erratic. Bromine oxidized the disodium salt 3 of dinitroethane into 1,2-dinitroethylene 4 but transformed the disilver salt 5 of tetranitroethane into 1,1,2-tri- bromo-1,2,2-trinitroethane 6.[8,10] Chlorine and the dipotassium salt 7 of α,α'-dinitrosuccinonitrile gave

1,2-dichloro-1,2-dicyano-1,2-dinitroethane 8.[11]

$$Na^+ \ ^-O_2N{=}CHCH{=}NO_2^- \ ^+Na \xrightarrow[-50^oC]{Br_2} O_2NCH{=}CHNO_2$$

3 4

$$Ag^+ \ ^-O_2N{=}C(NO_2)C(NO_2){=}NO_2^- \ ^+Ag \xrightarrow{Br_2} Br_2C(NO_2)C(NO_2)_2Br$$

5 6

$$K^+ \ ^-O_2N{=}C(CN)C(CN){=}NO_2^- \ ^+K \xrightarrow{Cl_2} (ClC(NO_2)CN)_2$$

7 8

Results. In contrast with the chlorination reaction 7 → 8, bromine and the dipotassium salt 7 gave the potassium salt 9 (21%) of nitroketosuccinonitrile along with potassium bromide (77%). The structure for the salt 9 was supported by elemental analysis and by infrared absorption at 2200 (w, cyano group) and 1645 cm^{-1} (m, carbonyl group in a salt of an α-nitroketone).[12] Other ir absorption at 1590 (s) and 1380 cm^{-1} (s) is characteristic of a nitro group. The salt 9 resisted attack by halogen, a property previously reported for the dipotassium salt 10 of tetranitroethane (prepared along with a mixed halogen from 1,2-dichlorotetranitroethane and potassium iodide).[8] In concentrated sulfuric acid at -40°, the salt 9 gave an intractable mixture, and in

methanol it was slowly converted into an unidentified solid, $C_6H_5N_3O_5K_2$, mp 276-277°C (dec).

$$\underline{7} \xrightarrow[-Br^-]{Br_2,\,0^\circ C} K^+[{}^-OC(CN)=C(CN)NO_2 \longleftrightarrow O=C(CN)C(CN)=NO_2^-]$$

$$\underline{9}$$

$$(ClC(NO_2)_2)_2 \xrightarrow[-ICl]{KI} K^+\ {}^-O_2N=C(NO_2)C(NO_2)=NO_2^-K^+$$

$$\underline{10}$$

Discussion. Electrophilic attack by halogen on a mononitronate salt is known to produce a gem-halonitro compound.[13] Apparently, similar reactions gave the dichloride 8 and 1,2-dichlorotetranitroethane 11 from the dinitronates 7 and 5.[8,11] An electron transfer from a nitronate anion to halogen can initiate these as well as

$$R_2C{=}NO_2^- \xrightarrow{X_2} R_2CXNO_2, \quad X = Cl, Br$$

$$\underline{5} \xrightarrow{Cl_2} ((O_2N)_2CCl)_2$$

$$\underline{11}$$

similar reactions, i.e., 3 → 4, 5 → 6, 7 → 8 and 7 → 9 by the formation of intermediate radical anions.[14] The intermediate 12 from the dinitronate 3 can afford the olefin 4 by an additional electron transfer and account for the formation of 1,4-dinitrobutadiene[14]

by coupling of intermediate 12 followed by an additional electron transfer and 1,2-elimination of dinitrogen tetroxide.

$$\underline{3} + Br_2 \xrightarrow{-50^{\circ}C} \underset{\underline{12}}{O_2N{=}CHCHNO_2} \xrightarrow{Br_2} \underline{4}$$

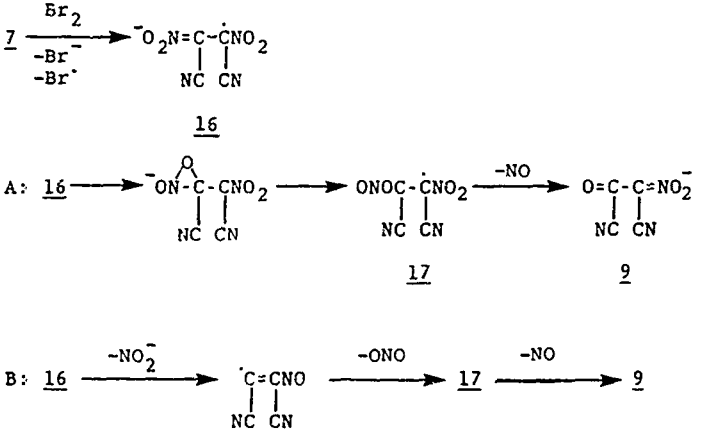
$$\underline{12} \longrightarrow \underset{\underline{13}}{{}^{-}O_2N{=}CHCH(NO_2)CH(NO_2)CH{=}NO_2^{-}}$$

$$\underline{13} + Br_2 \longrightarrow \underset{\underline{14}}{O_2NCH{=}CHCH{=}CHNO_2} + N_2O_4 + Br\cdot + Br^{-}$$

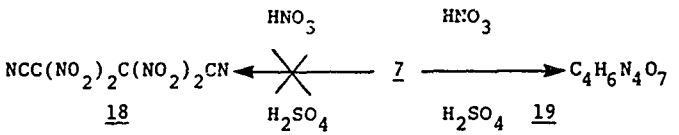
Ejection of a nitro group as a nitrite anion[15] from the intermediate radical anion 15 (generated from the dinitronate 5) can lead to the formation of the tribromotrinitroethane 6 on further reaction with bromine. An expected evolution of nitrogen oxides was not reported in the abstract.[8]

$$\underline{5} \xrightarrow[-Br^{-}\ -Br\cdot]{Br_2} (O_2N)_2\dot{C}C{=}NO_{NO_2} \xrightarrow{-NO_2^{-}} O_2NC{=}C(NO_2)_2 \xrightarrow[-Br\cdot]{2Br_2} \underline{6}$$

In the conversion of an intermediate radical anion 16 from the dinitronate 7 into the ketonitronate 9 a nitro group was the presumed source of the keto oxygen atom.[16] A differentiation between intramolecular and intermolecular creation of new carbon-oxygen bonding can not be made at this time; however, it was assumed that in either event isomerization of a nitro derivative into a nitrite ester occurred. There is precedent for both the thermal isomerization (Path A)[17] and also for expulsion of a nitrite anion followed by recombination and expulsion of nitric oxide (Path B)[3] to give an α-oxonitronate salt.



An investigation of the elimination of dinitrogen tetroxide from tetranitrosuccinonitrile 18[18] was thwarted when nitration of the dinitronate salt 7 failed to produce 18 and gave instead an unidentified compound 19.



Acknowledgement: Financial assistance was received from ONR.

Experimental.[19]

Potassium salt 9 of nitroketosuccinonitrile. To a suspension of α,α'-dinitrosuccinonitrile[11] (1.47g, 6 mmol) in anhydrous ether (50 ml) in a three necked round bottom flask equipped with a drying tube filled with Drierite and cooled to -5 °C, bromine (4.0 g, 24 mmol) was added dropwise with vigorous stirring over 45 minutes. After the mixture was stirred at 0 °C for 16 hours a colorless precipitate, 1.68 g, mp > 300 °C, was

isolated by filtration and dissolved in hot methanol (40 ml). Dry ether was added to precipitate potassium bromide, 0.54 g, 77%, with a confirmation of its identification by the precipitation of silver bromide on treatment with a solution of silver nitrate. Concentration of the mother liquor brought about the separation of the salt 9, 0.23 g (21%), mp 193-194 °C (dec) after recrystallization from methanol; ir (KBr): 2220 (w, CN), 1645 (m, CO or C=N), 1590 (s, NO_2), 1460 (m), 1380 (s, NO_2) and 1325 (m); calc'd for $C_4N_3O_3K$: C, 27.12; N, 23.72; O, 27.12; K, 22.02; found: C, 27.27, 27.07; N, 23.68, 23.59 (other samples gave found O, 28.83, 29.11 and K, 20.14).

Repeated recrystallizations of the salt 9 from methanol gave an unidentified colorless solid, mp 276-277 °C (dec); ir (KBr): 2210 (m, CN), 1710 (s, CO), 1440(w), 1360(s), 1300(m) and 1110(s); nmr(CH_3COCH_3 and DMSO-D_6): δ 2.9(s, 2) and 3.5 (s, 3); anal. calc'd. for $C_6H_5N_3O_5K_2$: C, 25.99; H, 1.80; N, 15.16; O, 28.88; found: C, 26.45, 26.54; H, 1.73, 1.69; N, 15.49, 15.39; O, 28.15, 28.42.

Attempted nitration of the salt 7. To a suspension

of the salt 7 (0.98 g, 4 mmol) in anhydrous methylene chloride (25 ml) at -35 °C concentrated sulfuric acid (5 ml) was added dropwise as a light green paste formed. A solution of concentrated sulfuric acid (2 ml) and fuming nitric acid (2 ml) was then added dropwise and the mixture held for 15 m at -30 °C before warming gradually to 20 °C. It was stirred for 30 m and the separated methylene chloride layer was dried (Na_2SO_4) and concentrated to leave a yellow gum. Trituration with tetrahydrofuran (0.5 ml) gave a yellow solid, 0.42 g (52%), mp 167-168 °C (dec) after recrystallization from acetic acid; ir(KBr): 3345(m), 3240(m), 1670(s), 1620(s), 1380(s), 1265 cm^{-1}(m); calc'd for $C_4H_6N_4O_7$: C, 21.62; H, 2.70; N, 25.22; O, 50.45; found: C, 22.14, 21.96; H, 2.78, 2.76; N, 25.59, 25.64; O, 47.94, 47.76.

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*. To whom correspondence should be addressed.

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19. Instruments included Perkin Elmer 237B and 521 grating i.r., Varian A-60, Bruker WP-80 and A.E.I. MS 30 double beam mass spectrometers. Elemental analyses were provided by Micro-Tech Laboratories, Skokie, Illinois.

O-CYANOMETHYLOXIME OF NITROGLYOXYLONITRILE

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The formation of the O-cyanomethyl ether 3 (a nitrolate ester) of nitroglyoxylonitrile oxime from iodoacetonitrile and silver nitrite (eq 1,2) offers a new preparation of a nitrolate ester independent of an α-nitronitronate ester or anhydride.[1-3]

$$ICH_2CN \xrightarrow{AgNO_2} \underset{1}{O_2NCH_2CN} \xrightarrow{AgNO_2} \underset{2}{AgON{=}C(NO_2)CN} \qquad (1)$$

$$\underset{2}{} \xrightarrow{ICH_2CN} \underset{3}{NCCH_2ON{=}C(NO_2)CN} \xrightarrow{H_2O} HOCH_2CN + \underset{4}{HON{=}C(NO_2)CN} \qquad (2)$$

Nitrosation of unisolated nitroacetonitrile 1[4] followed by alkylation of the nitrolate 2[5] by iodoacetonitrile accounted for the formation of the ether 3. Competitive alkylation at the oxime nitrogen atom was apparently retarded by an electron withdrawal into the cyano and nitro groups.[6] The liquid nitrolate ester 3 (44%) was the only product isolated; its structure assignment was supported by spectroscopy, elemental analysis and chemical reaction (eq 3).

$$3 + HOCH_2CN \longrightarrow NCCH_2ON{=}C(OCH_2CN)CN \qquad (3)$$

$$\underline{4} \dashrightarrow HCN + CO_2 + N_2O \qquad (4)$$

Warm water transformed the ether 3 into the O-cyanomethyl ether 5 (48%), mp 73-74°C,[1] of cyanomethyl cyanoformate oxime (eq 2 and 3). Its formation can be accounted for by a nucleophilic substitution of the nitro group in a reaction between the oxime ether 3 and the cyanohydrin of formaldehyde, a hydrolytic intermediate. The nitrolic acid 4 was undetected and was presumably hydrolyzed into hydrogen cyanide, carbon dioxide and nitrous oxide (eq 4).[7] The structure assignment for compound 5 was supported by spectroscopy and elemental analysis.

EXPERIMENTAL

Instruments included Perkin Elmer 237B and 521 grating ir, Varian T-60 and Bruker WP-30 nmr and Varian MS-30 spectrometers. Elemental analyses were obtained from Micro-Tech Laboratories, Skokie, Illinois.

O-Cyanomethyl ether 3 of nitroglyoxylonitrile oxime.-Iodoacetonitrile (20.04 g, 0.12 mole) was dissolved in 200 ml of dry ether in a 500 ml three-necked round-bottom flask equipped with a mechanical stirrer and reflux condenser. Silver nitrite (22.95 g, 0.15 mole) was added in one portion. After the mixture was heated at reflux temperature with vigorous stirring for 20 h it was cooled and filtered. The ether solution was dried ($MgSO_4$) and concentrated to give the oxime 3 as a yellow viscous oil (8.1 g, 44%). The oxime was eluted from a column (4 x 90 cm) of silica gel (100 g) by chloroform to give 6.8 g (37)%. Anal. calcd for $C_4H_2N_4O_3$: C,31.18; H,1.31; N,36.36; found: C,31.22; H,1.29; N,36.08; Ir(CH_2Cl_2):

3005(w,CH_2), 2220(w,C≡N), 1605(s,C=N), 1570 (s,NO_2) and 1340 cm $^{-1}$(m,NO_2); pmr ($CDCl_3$): δ 5.2 (s, not exchangeable with D_2O); ^{13}Cnmr ($CDCl_3$): δ 125.49(-N=C), 113.01(N<u>C</u>-CH_2), 103.24(=C-<u>C</u>N) and 63.89 ppm (OCH_2), split into a triplet in the coupled spectrum; m/e(70 ev)(%): 154(100) M^+, 153(40), 152(50), 138(90), 137(50), 127(80), 126(75) and 109(75).

<u>O-Cyanomethyl ether 5 of the oxime of cyanomethyl cyanoformate</u>.-A mixture of the oxime ether <u>3</u> (2 g, 12 mmole) and water (10 ml) was refluxed (25 h), cooled and filtered to give the ether <u>5</u> as a light yellow solid, 0.51 g (48%), mp 73-74°[1] after recrystallization from a mixture of ethyl acetate and hexane. Ir(CH_2Cl_2): 2250(w,CN) and 1615 cm^{-1} (m,C=N); pmr($(CD_3)_2CO$): δ 5.13(s,CH_2) and 5.26 (s,CH_2), neither exchangeable with D_2O); ^{13}Cnmr ($CDCl_3$ and $(CD_3)_2SO$): δ 138.28(N=C), 115.10(C≡N), 113.35(C≡N), 105.53(=C-<u>C</u>N), 60.93(OCH_2) and 54.42(OCH_2); m/e (70ev)(%): 164(15) M^+, 138(10), 134(20), 109(5), 107(10), 104(20), 94(90), 84(20) 80(80) and 79(100); anal. calcd for $C_6H_4N_4O_2$: C,43.91; H,2.46; N,34.14; found: C,43.96; H,2.38; N,34.04.

<u>Acknowledgement</u>. Financial support was received from the Office of Naval Research.

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directions have been repeated.

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Peroxide Oxidation of Diaminomaleonitrile and Derivatives

By Joseph H. Boyer*, V. T. Ramakrishnan and T. P. Pillai

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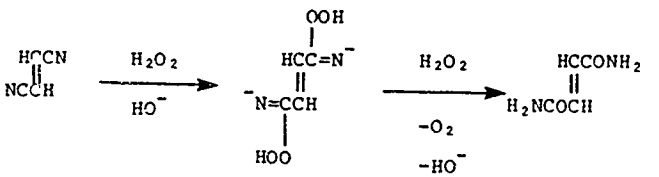
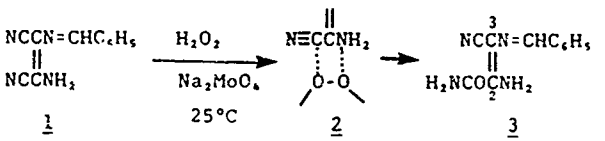
Diaminomaleonitrile (DAMN) and hydrogen peroxide in acetone produced oxamide in 80% yield. Hydrogen peroxide complexed with 1,4-diazabicyclooctane (DABCO) had no effect on DAMN but the monobenzylidene derivative of DAMN took up one equivalent of peroxide from DABCO•$2H_2O_2$ to give the monobenzylidene derivative 6 of E-1-cyano-2-carbamoyl-1,2-di-aminoethylene. The olefin 6 in dimethylsulfoxide slowly isomerized into its Z-form 3 and the reverse isomerization occurred in o-dichlorobenzene at 180°C. The mono-N-acetyl derivative of DAMN took up one equivalent of hydrogen peroxide to give an unassigned mono-N-acetyl derivative of 2,3,4-tri- amino-5-oxopyrroline in good yield.

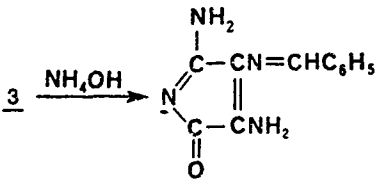
Introduction. An intermediate with peroxyimidic acid groups accounted for the Radziszewski reaction[2] whereby fumaronitrile and alkaline peroxide quantitatively produced the diamide of fumaric acid.[1] A regiospecific control was attributed to the intermediate 2 in the similar hydration of a cyano group in a mono imine derivative 1 of diaminomaleonitrile (DAMN) by aqueous hydrogen peroxide in alcohol. Cyclization of the amide 3 in warm ammonium hydroxide into a pyrrolone confirmed the cis-rela-

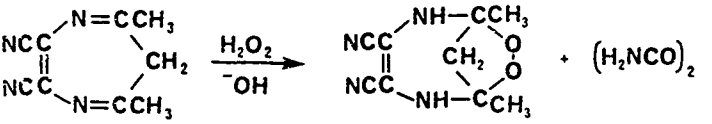
tionship between the carbamoyl and cyano substituents. Certain other mono- and bis-imines of DAMN similarly gave amides but N,N'-dibenzylidenediamine maleonitrile was unreactive toward peroxide and both N'-acetyl and N'-benzyl derivatives of the amine 1 gave unidentified material.[2]

On the other hand hydrogen peroxide in the presence of sodium hydroxide transformed the diazepine 4 (from DAMN and pentan-2,4-dione) into a bicyclic peroxide 5 (75%) and a trace of oxamide. In the absence of a base the reaction gave larger amounts of oxamide and trace amounts of the peroxide 5. The diazepine 4 was unreactive toward either m-chloroperbenzoic or trifluoroperacetic acids under mild conditions whereas more rigorous conditions brought about the formation of intractable material.[4]



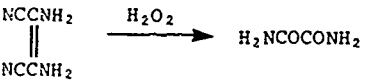






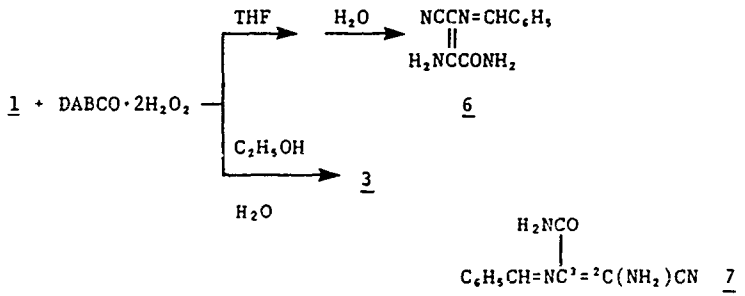
4 5

Results. Oxamide was produced from hydrogen peroxide and DAMN in acetone, methylene chloride, chloroform or methanol but not in tetrahydrofuran (THF) or acetonitrile. Peracetic, trifluoroperacetic, m-chloroperbenzoic (MCPBA) and monopermaleic acids with DAMN gave intractable product mixtures (Table).



DAMN

The complex DABCO•2H_2O_2 slowly but efficiently converted the N-benzylidene derivative 1 in THF into an intermediate which rapidly gave the mono amide 6 on the addition of water; trace amounts of the isomeric amide 3 were detected. On storage in dimethyl sulfoxide at room temperature for five weeks the amide 6 isomerized into amide 3; the reverse isomerization 3 → 6(77%) occurred in o-dichlorobenzene at 180°C.[5]



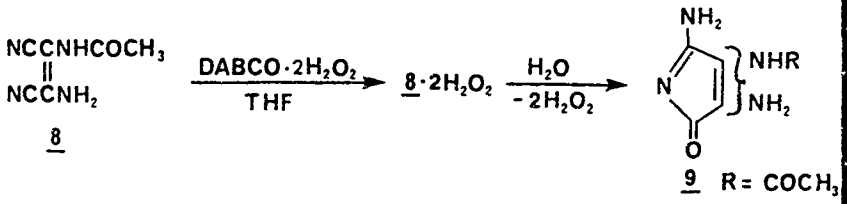
Investigations on oxidation of DAMN and various derivatives and summarized in the Table.

Table

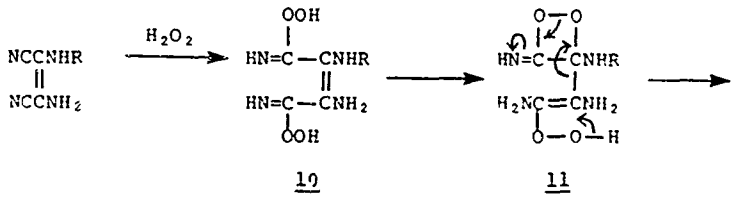
The structural assignment for amide 6 was supported by ^{13}C-nmr chemical shifts (ppm) at 151.25 (C-2) and at 94.58 (C-3), their close association with 152.11 (C-2) and 92.70 (C-3) reported for the amide 3, and the chemial shift differences in C-2 and C-3: 56.67 for amide 6 and 59.41 for amide 3 which agree with the calculated difference of 60.1 and do not support the alternative assignment of amide 7 for which a chemical shift difference in C-2 and C-3 of 11.7 was calculated.[3]

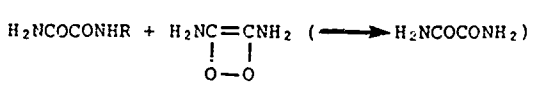
N-acetyldiaminomaleonitrile[6] 8 and DABCO·2H$_2$O$_2$ gave an intermediate insoluble in chloroform. It was assumed to be a complex between compound 8 and hydrogen peroxide since absorption for the cyano group at 2195 cm^{-1} was detected and treatment with water gave a mono-N-acetyl derivative 9 of 2,3,4-triamino-5-oxopyrroline, a structure supported by ir absorption at 1745 and 1696 cm^{-1} for cyclic and acyclic amide

carbonyl groups, nmr signals at δ 2.04 (CH_3) and at δ 5.4 and 2.9 (NH, exchangeable with D_2O), m/e (70 ev) 168 M^+, and elemental analyses. The oxopyrroline 9 remained unchanged in the presence of hydrogen peroxide at 25°C for 24 h; however, after 21 days it was transformed into oxamide.

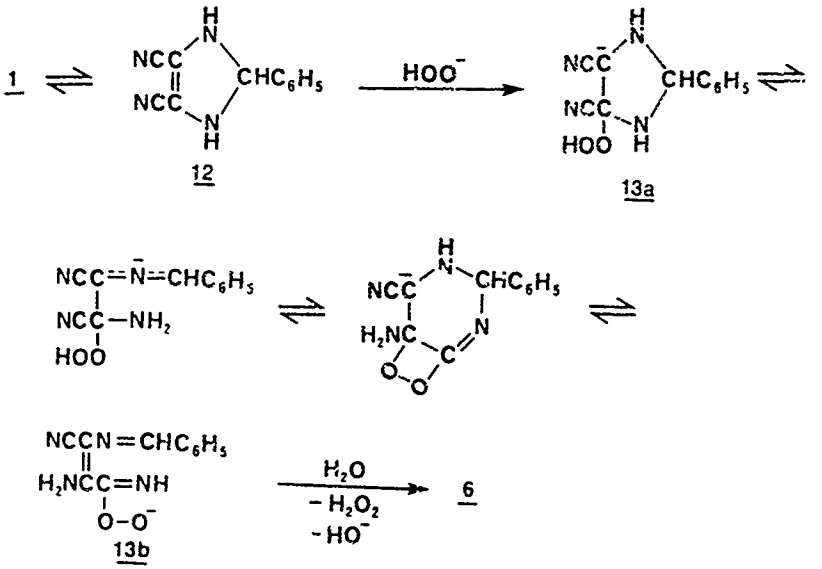


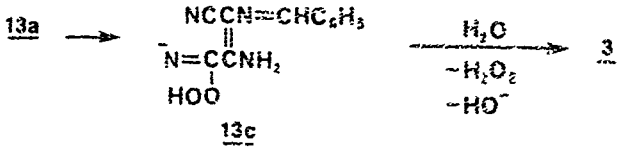
Discussion. A Radziszewski intermediate 10 and its ring isomer 11 accounted for the formation of oxamide from DAMN and hydrogen peroxide (90%) in acetone. An alternative cyclization of intermediate 10 (R = $COCH_3$) with expulsion of hydrogen peroxide (its assumed oxidation into oxygen resembled the last step of the Radziszewski reaction) accounted for the formation of the N-acetyl derivative 9 of triaminooxopyrroline.





Conversion of the mono benzylidene derivative 1 of DAMN into the geometrically isomeric amides 3 and 6 is obviously not controlled by the previous intermediate 2. An apparent need for intermediate equivalency between C2-C3 atoms and their transformation into transient sp³ carbon atoms can be satisfied by a peroxide attack on either of these two atoms in the dihydroimidazole cyclic tautomer 12 to produce the anion 13a. Ring-chain isomerization into the peroxyimidate anion 13b and hydrolytic reduction (completion of a Radziszewski reaction) can account for the formation of amide 6.[7] On the other hand an isomerization 13a → 13c (see scheme) afforded amide 3 by completion of a Radziszewski reaction. Unlike its isomer 3, which underwent cyclization into a 5-oxopyrroline compound 6 was unaffected by similar treatment with ammonium hydroxide.





EXPERIMENTAL

Instruments included Perkin Elmer 237B and 521 grating i.r., Varian A-60 and T-60 and Bruker WP-80 and A.E.I. MS30 double-beam mass spectrometers. Yields were based on starting materials consumed. Elemental analyses were provided by Micro-Tech Laboratories, Skokie, Illinois. DAMN was commercially available.

DAMN and Hydrogen Peroxide. After a solution of DAMN (1.0 g, 10 mmol) in tetrahydrofuran (THF) (50ml) was treated with hydrogen peroxide (90%, 0.9 ml, 32 mmol) and stirred at room temperature for 16 hours only DAMN was detected by tlc. The solvent was removed in a rotary evaporator (< 45°C) and chloroform was added to the viscous residue. A violent reaction occurred within a few minutes and oxamide (1.4 g , 80%) precipated; dec above 350°C.[8] satisfactory titration of oxalic acid derived from the amide against permanganate; ir (KBr): 3360 (br.s,NH), 3160, 1650 (br.s,CO), 1340 and 1095 cm^{-1}; m/e (70ev) (%): 88(100) M^+, 70(60), and 60(50).

A solution of DAMN (2.0 g, 20 mmol) in acetone (30 ml) with hydrogen peroxide (90%, 10 ml) was heated at reflux for 20 h to give oxamide (1.06 g, 78%).

N-Acetyldiaminomaleonitrile and DABCO•2H_2O_2. A solution of N-acetyldiaminomaleonitrile[3] (1.0 g, 6.7 mmol) in THF (100 ml) was stirred with DABCO•2H_2O_2[9] (3.0 g, 16.7 mmol) at room temperature for 16 hours. Filtration separated the unreacted DABCO•2H_2O_2 as a colorless solid (1.6 g). THF was removed by evaporation; the residue was triturated with chloroform and collected by filtration as a light yellow solid (1.5 g., mp 200-202°C, dec.) which dissolved in water to give, after a few minutes, an unassigned mono-N-acetyl derivative 9 of 2,3,4-triamino-5-oxopyrroline as a yellow solid, 0.65 g., mp > 260°C after recrystallization from dimethyl formamide; ir (KBr): 3100-3400, 1745 (s), 1696 (m), 1620-1650 (s), 1520 (s), 1400 (s), 1365 (w), 1285 (m) cm^{-1}; m/e (70 ev) (%): 168 (15) M^+, 126 (63), 71 (42), 43 (100); nmr (DMSO-d_6): δ 2.04 (s, CH_3), 5.4 and 9.23 exchanged with D_2O; found: C, 42.74; H, 4.86; N, 33 03; $C_6H_8N_4O_2$ requires C, 42.86; H, 4.80; N, 33.32%.

Benzylidenediaminomaleonitrile. Diaminomaleonitrile (8.0 g, 74 mmol), benzaldehyde (11.0 g, 104 mmol) and a few drops of trifluoroacetic acid in methanol (200 ml) was stirred for 16 hours. The product 1, partially soluble in methanol was obtained quantitatively (14.3 g) on concentration of the solvent; mp 198-200 °C (dec)[3]; ^{13}C-nmr(DMSO-d_6): δ 102.81, 113.74, 114.42, 126.96, 128.75, 129.04, 131.52, 135.55, 155 23.

DAMN and permaleic acid. A solution of hydrogen peroxide (90%, 7.0 g, 185 mmol), 1,2-dimethoxyethane (150 ml) and maleic

anhydride (24.0 g, 250 mmol) was heated to reflux, treated with a solution of DAMN (2.0 g., 18.5 mmol) in dimethoxyethane and heated at reflux for 16 hours. Solvent was removed and the reside diluted with water and extracted with ethyl acetate. The organic layer was washed with sodium carbonate solution, dried ($MgSO_4$) and removed to leave a residue in trace amount. Combined yields from several runs were chromatographically separated from a column of silica gel. Elution with chloroform gave 2-amino-3,5,6-tricyanopyrazine, mp 220-222°C (dec)[8] (ethyl acetate-chloroform) and cyanoformamide, mp 60-62°C[10](ethyl acetate-chloroform); ir (CH_2Cl_2): 3485 (m), 3370 (m), 2235 (w), 1725 (s), 1592 (m), cm^{-1}; m/e (70 ev): 70 M^+.

Benzylidendiaminomaleonitrile and DABCO•$2H_2O_2$ A solution of benzylidenediaminomaleonitrile[3] (1.0 g, 5 mmol) in THF (50 ml) was treated with DABCO•$2H_2O_2$ (2.0 g, 10.7 mmol) and stirred at room temperature for 30 days. Solvent removal, treatment of the residue with water, and filtration gave a solid, 0.7 g (two spots tlc). The E-monoamide 6 of benzylidenediaminomaleonitrile separated from a solution of the mixture in dimethyl formamide and tetrahydrofuran; mp 225-7°C(dec); ir (KBr): 3420, 3200-3300, 2185, 1695, 1610, 1560, 1420 cm^{-1}; m/e(70 ev) (%): 214 (55) M^+, 213 (28), 197 (4), 196 (25), 170 (10), 169 (6), 143 (8), 142 (25), 138 (8), 137 (100), 120 (40), 117 (14), 116 (22), 115 (12), 111 (12), 106 (10), 104 (20), 95 (14), 91 (8), 90 (23), 89 (26), 78 (22), 77 (20); found: C, 61.31; H, 4.79; N, 25.90; $C_{11}H_6N_4O$ requires C, 61.67; H, 4.71; N, 26.15%.

The Z -monoamide 3 of benzylidenediaminomaleonitrile was detected by tlc comparison with an authentic sample;[3] mp 211-212°C (dec), lit.[3] mp 197-9°C (dec); m/e(70 ev) (%): 214 (56) M^+, 213 (28), 197 (4), 196 (26), 170 (12), 169 (8), 143 (11), 142 (36), 138 (8), 137 (100), 120 (45), 117 (18), 116 (30), 115 (16), 111 (16), 106 (9), 104 (20), 95 (14), 91 (10), 90 (25), 89 (34), 78 (20), 77 (18); ^{13}C-nmr (DMSO-d_6): δ 92.65, 115.25, 128.17, 128.70, 130.26, 136.48, 150.18, 152.32, 164.51.

Both tlc and ^{13}C-nmr revealed an isomerization of the amide 6 into amide 3 in dimethyl sulfoxide-d_6 (solvent used for nmr) in about 30 hours to an extent of 30%. After 5 weeks the isomerization reached 50%. Both isomers 6 and 3 were detected by ^{13}C-nmr: 92.58(3), 94.58(6), 114.14(6), 115.29(3), 127.44(6), 128.17(3), 128.65(3), 128.90(6), 130.17(3,6), 136.19(6), 136.49(3), 148.39(6), 150.03(3), 151.25(6), 152.52(3), 163.09(6), 164.61(3). The assignments for compounds 6 and 3 were determined from two spectra from the same solution, one taken when the solution was freshly prepared and one after an interval of 5 weeks.

When the reaction was carried out in aqueous ethanol (90%) benzylidenediaminomaleonitrile and the DABCO•$2H_2O_2$ at room temperature for 14 days furnished the amide 3 in 65% yield.

After treating the amide 3 (200 mg) with DABCO•$2H_2O_2$ complex (500 mg) in tetrahydrofuran at room temperature for 40 hours the presence of the amide 6 was detected (tlc).

Heating a sample of amide 3 (200 mg) at 180°C in o-dichlorobenzene (10 ml) for 2 hours afforded the fumaramide 6 in 75% yield, identified by tlc, mp and mixture mp.

The amide 6 (10 mg) remained unreactive to ammonium hydroxide (28%, 3 ml) after 3 h at 25°C and was quantitatively recovered. Under similar conditions the amide 3 cyclized into the oxopyrroline 9[3].

Acknowledgement: Financial support was received from ONR.

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Table

DAMN Derivatives, $H_2NC(CN{=}C(CN)NRR'$, and Peroxides

R R'	Peroxide Solvent	Hours[a] t, °C	Product, % yield
H H	H_2O_2[b] CH_2Cl_2	0.2 25	$(CONH_2)_2$[c] 43
H H	H_2O_2[b] $CHCl_3$	0.1 25	$(CONH_2)_2$[c,d,e] 80
H H	RCO_3H[f] CH_2Cl_2	1 39	$NCCONH_2$, 10% mp 60-62°[g]
CH_3CO H	H_2O_2[b] CH_3OH	40 25	$(CONH_2)_2$[c] 31
$=C(C_6H_5)_2$	CF_3CO_3H CH_2Cl_2	1 39	Trace unidentified
$=CHC_6H_4OCH_3$-p	H_2O_2[b] CH_3OH[h,i]	64 25	——[j]

[a]Time required for disappearance (monitored by tlc) of DAMN or a derivative. [b]Commercial reagent, 90% in 6-60 molar excess. [c]No other product detected by tlc. [d]Starting material detected by tlc. [e]Oxamide was not detected when DAMN was treated with either H_2O_2 or $DABCO{\cdot}2H_2O_2$ in THF; the latter gave an unidentified solid, mp 134-136°C. [f]Monopermaleic acid. [g]There was also a trace amount of 2-amino-3,5,6-tricyanopyrazine, mp 220-222°C(dec), previously obtained from DAMN and trifluoroperacetic acid (R. C. Begland, D. R. Hartter, D. S. Donald, A. Cairncross and W. A. Shephard, J. Org. Chem., 1974, 39, 1235).

[h]With a catalytic amount of NaOH. In the absence of alkali an intractable mixture was obtained. [i]Intractable mixtures were obtained from treatment with H_2O_2 in CH_3CO_2H, CF_3CO_2H, HNO_3, CH_3CN or THF or from treatment with MCPBA in $CHCl_3$ or CH_2Cl_2. Starting material was completely recovered after treatment with $DABCO \cdot 2H_2O_2$ in THF. [j]A trace amount of p-$CH_3OC_6H_4CH{=}NC(CN{=}C(NH_2)CONH_2$, mp 213-216°C.[3]

A 7-Azanorbornene from a Pyrrole and Tetracyanoethylene.

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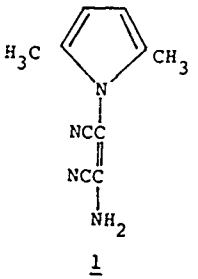
7-(Z-1',2'-Dicyano-2'-aminovinyl)-5,5,6,6-tetracyano-1,4-dimethylnorbornene 2 was obtained from the Diels-Alder addition of tetracyanoethylene to 1-(Z-1',2'-dicyano-2'-aminovinyl)-2,5-dimethylpyrrole 1.

The pyrrole ring has rarely functioned as a diene in a Diels-Alder reaction.[1,2] An addition of tetracyanoethylene[3] to 1-(Z-1',2'-dicyano-2'-aminovinyl)-2,5-dimethylpyrrole 1[4] occurred readily to produce 7-(Z-1',2'-dicyano-2'-aminovinyl)-5,5,6,6-tetracyano-1,4-dimethylnorbornene 2 in excellent yield.† A competitive substitution reaction[5] to give a tricyanovinyl derivative was not detected. Apparently the N-vinylamine substituent activated the pyrrole ring toward electrophilic attack (Scheme);[2] however, both maleic anhydride and diethyl butynedioate failed to react with the pyrrole 1.

Compounds 1 and 2 resembled diaminomaleonitrile in resisting oxidation by peroxides.[6] In other support for the adduct 2, ^{13}C nmr confirmed assignments for each of the sixteen carbon atoms;‡ pmr detected methyl, amino and olefinic protons in the ratio 3:1:1; ir showed expected absorption for C≡N, >C=C<, CH and NH bonds. A very rich mass spectra (M+ not observed) showed a prin-

cipal peak at 287 (M - HCN), minor peaks at 186 and 128 attributed to a retro-Diels-Alder reaction,[7] and a minor peak at 94 attributed to the dimethylpyrrole nucleus (C_5H_8N).



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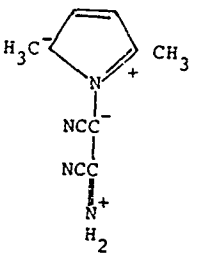

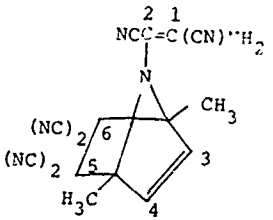

2

2 structures

Acknowledgement: Financial support was received from ONR.

Footnotes.

†Equimolar portions of compound 1 and TCNE were heated at reflux in tetrahydrofuran for 5 h. Evaporation of the solvent left the adduct 2 (88% yield), mp 254-255°C after recrystallization from a mixture of ethyl acetate and hexane. It gave satisfactory elemental analyses for C, H and N.

‡^{13}C nmr for adduct 2 in perdeuterated dimethylsulfoxide at either 25 or 70°C: δ 142.38 (C2); 133.51 and 133.14 ($\underline{C}CH_3$); 115.90, 115.05, 114.44, 113.65, 113.41 and 112.50 (CN); 106.73 (C3 and C4) 83.65 (C5 and C6); 81.89 (C1); 12.05 and 11.20 (CH_3).

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Nitrosamines and Nitramines from sec- and tert- aliphatic Amines. A preliminary report.

N-Alkyl(aryl)benzylamines 1-3 and N-methyl-β-phenethylamine 4 were nearly quantitatively transformed into nitrosamines 5-8 by nitrous acid in acetic acid buffered with sodium acetate.[1] The benzylamine 1 also was nitrosated by nitrosonium tetrafluoroborate under anhydrous conditions to give the nitrosamine 5 in high yield.[2]

$$\underset{\textbf{1-4}}{C_6H_5(CH_2)_nNHR} + NaNO_2 \xrightarrow[AcONa]{AcOH} \underset{\textbf{5-8}}{C_6H_5(CH_2)_nN(NO)R}$$

Reactants				Product	
R	n	No	Conditions	No	Yield,%
CH_3	1	1*	30 mol $^-NO_2$, 90°C, 3h	5	83
$C(CH_3)_3$	1	2*	6 mol $^-NO_2$, 25°C, 0.5H	6	89
C_6H_5	1	3*	6 mol $^-NO_2$, 25°C, 0.5h.	7	100
CH_3	2	4*	$^-NO_2$, 25°C,	8	100

$$2\ \mathbf{1} + NOBF_4 \xrightarrow[25^oC,\ 16\ h]{CHCl_3/N_2} 86\%\ \mathbf{5} + \mathbf{1}\cdot HBF_4 \xrightarrow{Na_2CO_3} \mathbf{1},\ 94\%.$$

N,N-Dimethylbenzylamine 9 and N,N-Dimethyl-β-phenethylamine 10 were efficiently tranformed into secondary nitrosamines 5, 6 by either nitrous acid or nitrosonium tetrafluoroborate.

$C_6H_5(CH_2)_nN(CH_3)_2 \longrightarrow C_6H_5(CH_2)_nN(NO)CH_3$

9 n = 1 → 5 n = 1

10 n = 2 → 8 n = 2

A Conditions: $NaNO_2$ (10 mol ratio), AcOH, AcONa, 90°, 3h.

Yields: 5, 68% (41% recovered 9).

8, 82% (50% recovered 10)

B Conditions: $NOBF_4$ (2 mol ratio), $CHCl_3/N_2$, 25°C, 70-100 h

Yields: 5, 61% (75% recovered 9) + C_6H_5CHO(tr)

8, 56% (73% recovered 10)

Peroxide efficiently oxidized the nitrosamines 5 and 8 into nitramines 11 and 12.[3]

$C_6H_5(CH_2)_nN(NO)CH_3 \longrightarrow C_6H_5(CH_2)_nN(NO_2)CH_3$

5 n = 1 → 11 n = 1

8 n = 2 → 12 n = 2

5 ⟶ 11, 90%

Conditions: H_2O_2 (30%), AcOH, 90°C, 7h.

8 ⟶ 12

Conditions	Yield,%
A. H_2O_2(30%), AcOH, 90°C, 7h.	78
B. m-$ClC_6H_4CO_3H$ $CHCl_3$,60°C, 48h	100 (recovered 8 35%)
C. H_2O_2(30%), CF_3CO_2H, CH_3OH, 70°C,3h.	40 (recovered 8, 56%).

The overall conversions of tertiary amines 9, 10 into nitramines 11, 12 are 65 to 80%.

Acetone cyanohydrin nitrate converted the secondary amines 1 and 4 into nitramines (50-80%); under similar conditions the tertiary amines 9 and 10 are unaffected.[4] For the transformation of acid-sensitive secondary amines into nitramines this procedure appears preferable to both the two step process of an aqueous nitrosation followed by oxidation and direct nitration in an acid medium.

$C_6H_5(CH_2)_nNHCH_3 \longrightarrow C_6H_5(CH_2)_nN(NO_2)CH_3$

1 n = 1 — 11 n = 1

4 n = 2 — 12 n = 2

Conditions: $(CH_3)_2C(CN)ONO_2$, no other solvent, 25°C, 6da(for 1), 2da (for 4)

Yields: 50% 11 and 50% $C_6H_5CH_2\underset{\displaystyle (CH_3)_2CCN}{\overset{\displaystyle |}{N}}CH_3$

50% 12 and trace of $C_6H_5CH_2CH_2\underset{\displaystyle (CH_3)_2CCN}{\overset{\displaystyle |}{N}}CH_3$

Nitramines were not detected from amines 1, 4, 9 or 10 when treated with nitronium tetrafluoroborate in concentrated sulfuric acid or in 1,2-dichloroethane or with mixtures of nitric and sulfuric acids; ring nitration occurred instead. Similar results were obtained from nitric acid (d 1.5).[5].

An evaluation of the preparation of sec-nitrosamines for oxidation into nitramines from corresponding tert-amines in a mixture of nitric and hydrochloric acids is continuing. This method was first reported by Japanese workers.[6]

$$R_2NCH_2R \xrightarrow[HCl]{HNO_3} R_2NNO \xrightarrow{[O]} R_2NNO_2$$

References and Notes

* Aldrich Chemical Company, Milwaukee, Wisconsin.

1. W. Lijinsky and G. M. Singer, Internation Agency for Research on Cancer Publication No. 9, 111 (1975).
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   The best yield of dimethylnitrosamine from dimethylamine and nitrous acid was obtained at pH 5. The yield was 2% at pH 1 and 0% at pH 11.

   $$(CH_3)_2NH + NaNO_2 \xrightarrow[\text{4h, 100°C}]{HClO_4} (CH_3)_2NNO$$
   0.05 m 0.25 m pH 5 quantitative

2. G. Olah, L. Noszko, S. Kuhn and M. Szelke, Chem. Ber. 1956, 89, 2375. Each of five sec-aliphatic amines and nitrosonium tetrafluoraborate in ether for 10 m gave the expected nitrosamine. Yields were 78-88%.

   $$2\ R_2NH + NOBF_4 \longrightarrow R_2NNO + R_2NH\cdot HBF_4$$

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